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ON THE ADSORPTION OF WATER VAPOR, CARBON DIOXIDE AND CERTAIN SUBSTANCES IN AQUEOUS SOLUTION BY FINELY DIVIDED QUARTZ.

A Dissertation presented to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy.

By

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1901

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78096

Acknowledgement.

I desire to express my obligation to Professor J. S. Ames for his kindly interest and numerous valuable suggestions throughout the progress of this work. To Professor H. C. Jones and Dr. N. E. Dorsey I am also deeply indebted for their kindness and assistance in various ways and for valuable criticism.

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ON THE ADSORPTION OF WATER VAPOR, CARBON DIOXIDE AND CERTAIN SUBSTANCES IN AQUEOUS SOLUTION BY FINELY DIVIDED QUARTZ.

Introduction.

Solid bodies possess the property of retaining upon their surfaces small quantities of gases or dissolved substances with which the surface of the solid is in contact. To this phenomenon, which relates only to surface conditions Dubois-Reymond applied the term "adsorption", to distinguish it from "absorption", - a term which had already been used to designate the solution of gases in liquids.

Adsorption, then, may be looked upon as the condensation of a small quantity of the adsorbed substance upon the surface of a solid. In the case of a gas, the density of the gas is greater on the surface of the solid than at a small distance outside. This is shown to be true by the fact that the mass of gas which is contained in a given volume at a definite temperature and pressure is greater when the volume of gas is distributed through the interstitial

space of a finely divided solid, than when simply confined by the boundary walls of the volume. Furthermore, when a solution of known concentration is shaken with a finely divided solid, the concentration of the clear supernatant solution is diminished. But since the dissolved substance is confined to a definite volume, namely the volume of solution used, it follows that the concentration of the solution constituting the film over the surface of the solid must have increased.

It is not at all probable that the same molecules continually constitute the adsorbed portion of the surrounding medium while a definite condition of equilibrium is being maintained. Just as in the case of a saturated vapor in contact with its liquid, there is every reason to suppose that the adsorbed molecules are being replaced continually by others that strike the surface of the solid under conditions that are momentarily more favorable for retention. By changing the concentration or the temperature, equilibrium is temporarily destroyed, and the mass of substance adsorbed changes until equilibrium is once more established under the new conditions.

HISTORICAL SKETCH OF ADSORPTION.

Adsorption phenomena have long been known and were early made the subject of a number of investigations, which were, however, mainly qualitative. There has been considerable controversy until recently as to whether the phenomena were truly physical in their nature, or were due to chemical combination. Such discussions were usually complicated by the consideration of systems in which chemical reactions undoubtedly did take place to some extent. But as we shall see later, the phenomena may readily be observed in systems whose components are generally admitted to undergo no chemical reaction.

Lowitz observed, as early as 1791, that wood charcoal has the ability to remove coloring matter from liquids; and Figuier, in 1810, showed that animal charcoal was even more active in this respect. Payen[*] found that charcoal removed not only coloring matter but lime as well, and Graham[*], in

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[*] Ann. de Chim. et de Phys. 21, 215, 1822.

[*] Pogg. Ann. 19, 139, 1830.

1830, held this action to be a general one, since he observed adsorption by charcoal in the case of a large number of salts. Many experiments of a qualitative nature were made later by various observers, showing that other solids possess the same properties as charcoal, though not to so great an extent.

Adsorption of Gases.

Investigations on the adsorption of gases were undertaken by Fontaine as early as 1777, and a great deal of work has been done on this branch of the subject. A very good bibliography is given in a recent article by Mülfarth* ,whose work, in addition to that of Bunsen*and Kayser** constitutes the more important contributions from the standpoint of the present investigation, which deals with adsorption by finely divided but non-porous solids. Adsorption by charcoal has

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(*) Ann. der Phys. (4) 3, 328, 1900.

(*) Wied. Ann. 20, 545, 1883; 22, 145, 1884; 24, 321, 1885; 29, 161, 1886.

(**) Wied. Ann. 15, p. 624, 1882.

received a great deal of attention, but the results of different investigators can hardly be compared on account of the lack of knowledge regarding the amount of surface presented by this substance.

Bunsen determined the adsorption of carbon dioxide on the surface of bundles of glass threads, the surface area of which he was able to compute approximately by determining the number, length, and average diameter. He found that adsorption went on for months before reaching a state of equilibrium. This is exactly opposite to the results obtained by other early investigators, who found that adsorption proceeded quite rapidly and was complete in a few hours or at most in a few days. These results were, however, nearly all obtained with charcoal, while Bunsen was working with glass threads, and, therefore, the conditions were different.

Mülfarth, in a paper which appeared during the progress of this work, states that the adsorption of carbon dioxide by dry powdered glass has reached a condition of approximate equilibrium at the end of one or two hours, so that Bunsen's conclusions in this respect appear to be in error. In the presence of moisture several days are required, although the amount adsorbed is practically the same in

both cases. Mülfarth states that the adsorption of carbon dioxide by powdered glass follows approximately Henry's law for the solution or adsorption of gases in liquids; that is, that the weight of gas adsorbed is proportional to its partial pressure in the region immediately about the adsorbing solid. The results obtained by Mülfarth, however, show a relation between the pressure p of the gas and the amount adsorbed g of the form

$$g = \alpha + \beta p$$

where α and β are both positive quantities, while if Henry's law applies,

$$g = \beta p.$$

Mülfarth's results are for comparatively high pressures of carbon dioxide, the lowest being about 140 mm. of mercury. We are consequently unable to conclude from his results anything regarding what takes place at lower pressures, such as in air, for example, unless we accept results obtained by unjustifiable exterpolation; for, according to Mendeleeff, the partial pressure of carbon dioxide in the atmosphere does not exceed 4 ten-thousandths of an atmosphere, or 0.3 mm. of mercury.

Adsorption of Water Vapor.

Few quantitative experiments on the relation between the vapor pressure and the amount of water appear to have been made. Bunsen (Wied. Ann. 24, 1885, 322) investigated the adsorption of water vapor by first exposing glass threads to saturated air and then passing dry air over the glass threads at various constant temperatures, noting the total amount of water removed at each temperature. From these investigations he calculated the total thickness of the water film at different temperatures, the surface area of the glass threads being calculated from previous measurements.

Warburg and Ihmori (Wied. Ann. 27, 1886) enclosed a delicate balance in an exhausted receiver so arranged that it could be connected at pleasure with vessels containing strong sulphuric acid or water. The weight of the film deposited on a this glass bulb suspended from a balance was determined and in this manner they were able to investigate the relation between the amount of water adsorbed and the va-

por pressure. They found that washing the glass bulb with boiling water before the experiment greatly diminished the thickness of the film deposited.

Adsorption of Dissolved Substances.

A general historical account of investigations on the adsorption of dissolved substances up to the year 1890 may be found in Ostwald's Lehrbuch der Allgemeine Chemie, Vol.I. These investigations nearly all deal with adsorption by wood or bone charcoal, substances which, while showing marked adsorption effects, are poorly suited to quantitative investigations of the subject, owing to the great difficulty in obtaining uniform samples. The complex nature of the substances also makes chemical reactions between the charcoal and the adsorbed substance exceedingly probable. In fact, Graham (Pogg. Ann. 19, p. 139, 1830) whose experiments are among the most extensive of those employing animal charcoal satisfied himself that chemical action did take place, and was inclined to consider the whole effect as being largely due to chemical action when this substance is employed.

In his Lehrbuch Ostwald mentions a series of experi-

ments conducted in his laboratory by A. Kelberin and himself. Animal charcoal was treated with a given amount of concentrated solution of a certain substance and allowed to stand for several days, when the concentration of the solution was compared with its original concentration. A given amount of water was then added to the solution in contact with the charcoal, which was then allowed to stand until equilibrium had once more been established, when the concentration was again determined. A series of dilutions were made in this manner, and it was found that the concentration of the solution was greater after dilition than would result from the simple dilution of the solution when not in contact with the charcoal. Plotting the amounts of water as abscissas and the quantity adsorbed as ordinates in a rectangular system of coordinates, the resulting curve was found to be approximately hyperbolical in form. No definite relations, however, were apparently obtained and the results of the investigation do not appear to have ever been published in detail.

Van Bemmelen (Jour. prakt. Chem. 23, 324, 1881) appears to have been the first to investigate the adsorption of salt and acid solutions in a quantitative way. He worked with sulphuric, nitric and hydrochloric acids and their

three potassium salts. He used amorphous silicon dioxide as the adsorbing substance, prepared by precipitation from soluble silicates by hydrochloric acid. Ten grams of the amorphous silica were added to each 100 c.c. of the solution. Normal, half-normal, and fifth-normal solutions were employed, and he found that the amount adsorbed was directly proportional to the concentration of the solution.

Schmidt (Ztschr. phys. Chem. 25, 56, 1894) has also investigated quantitatively the adsorption of dissolved substances by animal charcoal, cellulose and amorphous silica. Potassium chloride was the only solution employed when amorphous silica was used as the adsorbing agent. His results, while showing irregularities, appear to indicate a relatively greater adsorption as the concentration diminishes, although Schmidt concludes that adsorption is directly proportional to the concentration.

Kellner (Dissert. Strassburg, 1895. Abst. Ztschr. phys. Chem. 20, 655, 1896) has investigated the adsorption of very dilute acid and alkaline solutions by platinum black using the conductivity method. No quantitative results are, however, given in the abstract, and the original publication has not been accessible to me.

OBJECTS OF PRESENT INVESTIGATION.

The following were the principal objects of the present investigation:

FIRST - the quantitative investigation of the amount of adsorption occurring in aqueous solutions of the chlorides, carbonates and hydroxides of sodium potassium and ammonium, when in contact with finely divided quartz.

SECOND - the influence of concentration on the amount of adsorption, particularly in dilute solutions.

THIRD - the influence of temperature on the amount of adsorption.

FOURTH - the investigation of the adsorption of carbon dioxide at its partial atmospheric pressure.

FIFTH - the investigation of the relation between the vapor pressure of water and the amount of water adsorbed at ordinary temperatures.

SELECTION AND PREPARATION OF ADSORBING SUBSTANCE.

Quartz was selected in this investigation as the adsorbing substance for two reasons: First, it is one of the most insoluble substances known that can be conveniently obtained in a fine state of division; secondly, since it constitutes a large percentage of the minerals making up the soil, results obtained with this material would be of direct application to investigations relating to the retention of fertilizers or other soluble substances in cultivated soils.

The material principally used was from a vein of pure quartz in Lancaster county, Pennsylvania. This material is crushed to a fine powder in large quantities for the purpose of manufacturing porcelain. On examination the material was found to contain a small amount of chlorides, carbonates and bicarbonates, so that a thorough washing was necessary before the material could be used for adsorption investigations.

The washing of the quartz was done in the following manner: About 150 grams of the material was placed in a

bottle with an equal amount of distilled water, acidulated with hydrochloric acid and shaken in a mechanical shaker for several hours. (See Fig. I.) The bottles were then placed in the centrifugal apparatus shown in Figure II. and rotated rapidly for several minutes until practically all the fine material was thrown out of suspension when the super-natant liquid was decanted. Fresh distilled water was added and the operation repeated, until the specific electrical resistance of the decanted water was from 100,000 to 200,000 ohms, when the quartz was removed from the bottles, dried thoroughly at 110° C. and was then ready for use.

The centrifugal apparatus shown in Figure II. was of material assistance in the washing operations, as the suspended quartz could with its aid be thrown down in about ten minutes, whereas twenty-four hours would have been necessary had simple subsidence been employed. As will be seen from the figure, the centrifugal apparatus consists of a Holtzer-Cabot 16-inch, 110 volt fan motor placed with its shaft vertical, to which the frame-work, carrying two trunnioned racks for the shaker bottles, is attached.

In some later experiments in which the adsorption of salts in aqueous solution was being investigated by the dif-

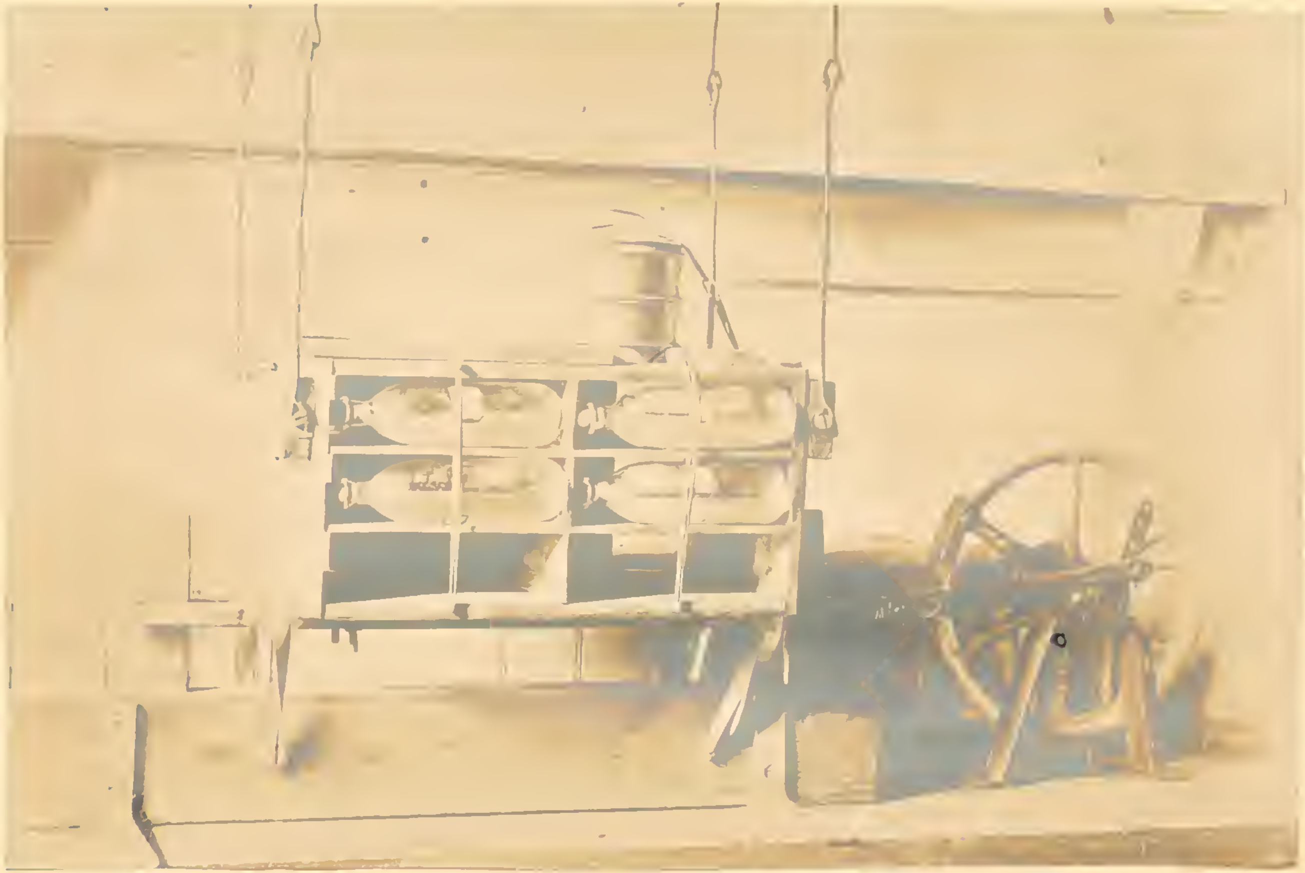


Fig 1 Mechanical shaker used in mixing yeast

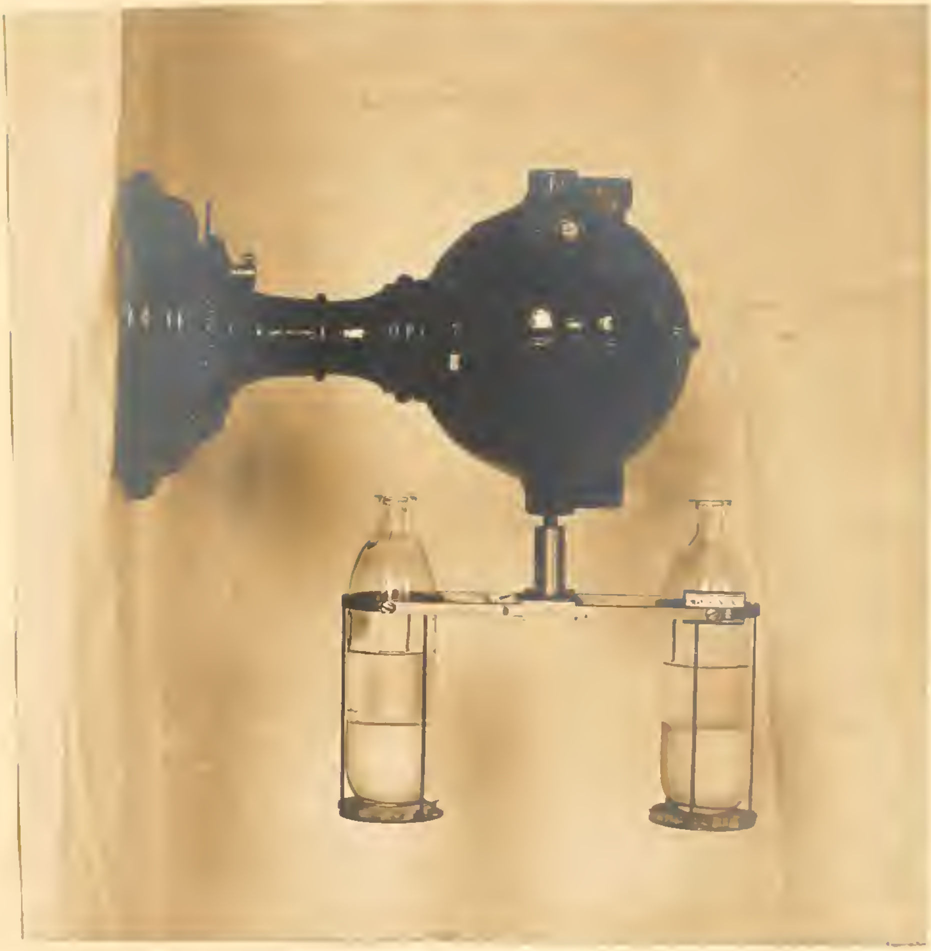


Fig 2 - Centrifugal apparatus used [illegible]
[illegible]

ference of the electrical conductivity of the solution before and after adsorption, it was found necessary to wash the quartz still more thoroughly than could readily be done by the method just described. Accordingly, the apparatus illustrated in vertical section in Figure 3 was constructed for this purpose. This apparatus consists of a nickel plated brass tube about 4 centimeters in diameter and 10 centimeters long, provided at its lower end with a beveled ring of such diameter as to fit tightly around the upper end of a Gooch platinum crucible. The collar is extended a short distance below the tube, and fits into another section of the tube closed at its lower end, as shown in the figure. The upper part of the apparatus is filled with the powdered quartz to be washed, and distilled water is added. Two pieces of this apparatus are then placed in the trunnioned racks of the centrifugal apparatus shown in Figure 2, and rotated until the water is thrown out of the quartz into the receptacle below. In this way it was possible to wash the material practically free from dissolved substances in a comparatively short time.

A microscopic examination of the quartz showed the grains to be sharp and angular, free from seams and fis-

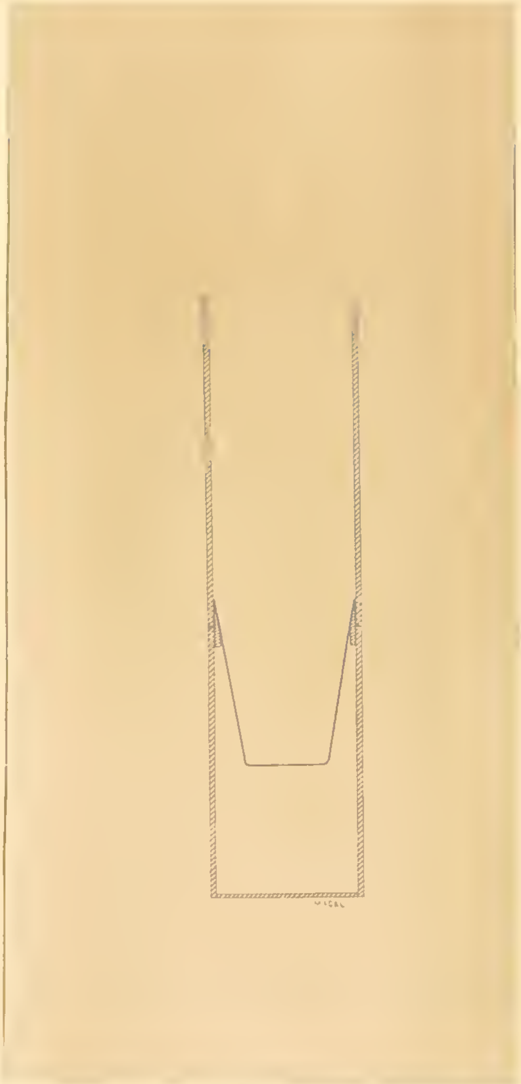


Fig 3 - Vertical section of apparatus for measuring [illegible] of the [illegible] [illegible]

sures, and practically free from occlusions.

Mechanical Analyses.

In order to obtain an idea of the amount of free surface in a gram of the powdered quartz, and also to determine as definitely as possible the character of the material employed, several mechanical analyses of the substance were made in the laboratory of the Division of Soils of the United States Department of Agriculture. This method of mechanical analysis consists in separating the soil grains into groups according to size and then determining by weight the relative percentages of the various groups. The separation of the finer grains is obtained by sedimentation in water, the process being accelerated by the aid of a centrifugal apparatus similar to that shown in Figure 2. The larger grains are graded by means of seives and bolting cloths of suitable meshes.

The following is the mechanical composition of the quartz sand used in the preliminary investigations.

Diameter m.m.	Per cent.
1 -.5	2.
.5 -.25	63.
.25 -.1	35.

Quartz "A" used in the greater part of the determinations has the following composition, which is the mean of four determinations kindly made for me by Mr. A. H. Prince.

Diameter	Per cent.
.25 -.1	2.
.1 -.05	12.
.05 -.005	85
.005	1

ADSORPTION OF WATER VAPOR.

The object of this portion of the investigation was to determine the relation between the partial pressure of aqueous vapor and the amount of water adsorbed. The appara-

tus shown in Figure 4 was used in the first series of experiments. This consisted of a train of four Jena glass flasks of about 100 c.c. capacity, provided with glass tube connections and rubber stoppers as shown in the figure, the whole apparatus being immersed in a thermostat at 30°C. Flasks A and B contained aqueous solutions of sulphuric acid of a concentration such that the partial pressure of the saturated vapor of the solutions corresponded to the partial vapor pressure desired. The flasks were also loosely filled with glass wool, which was kept moistened with the sulphuric acid solution, to insure the saturation of the air with vapor at the partial pressure of the solution. The quartz under investigation was placed in flask C, and flask D served as a trap to prevent any water condensed in the tube after leaving the thermostat from returning into the quartz. The safety-flask E prevented the filter water in the pump from striking back and filling the apparatus.

The operation consisted then in slowly drawing a stream of air through the two flasks containing sulphuric acid, the air thus receiving an amount of water vapor corresponding to the partial vapor pressure of the solution. The air then passed over into flask C and came in contact with

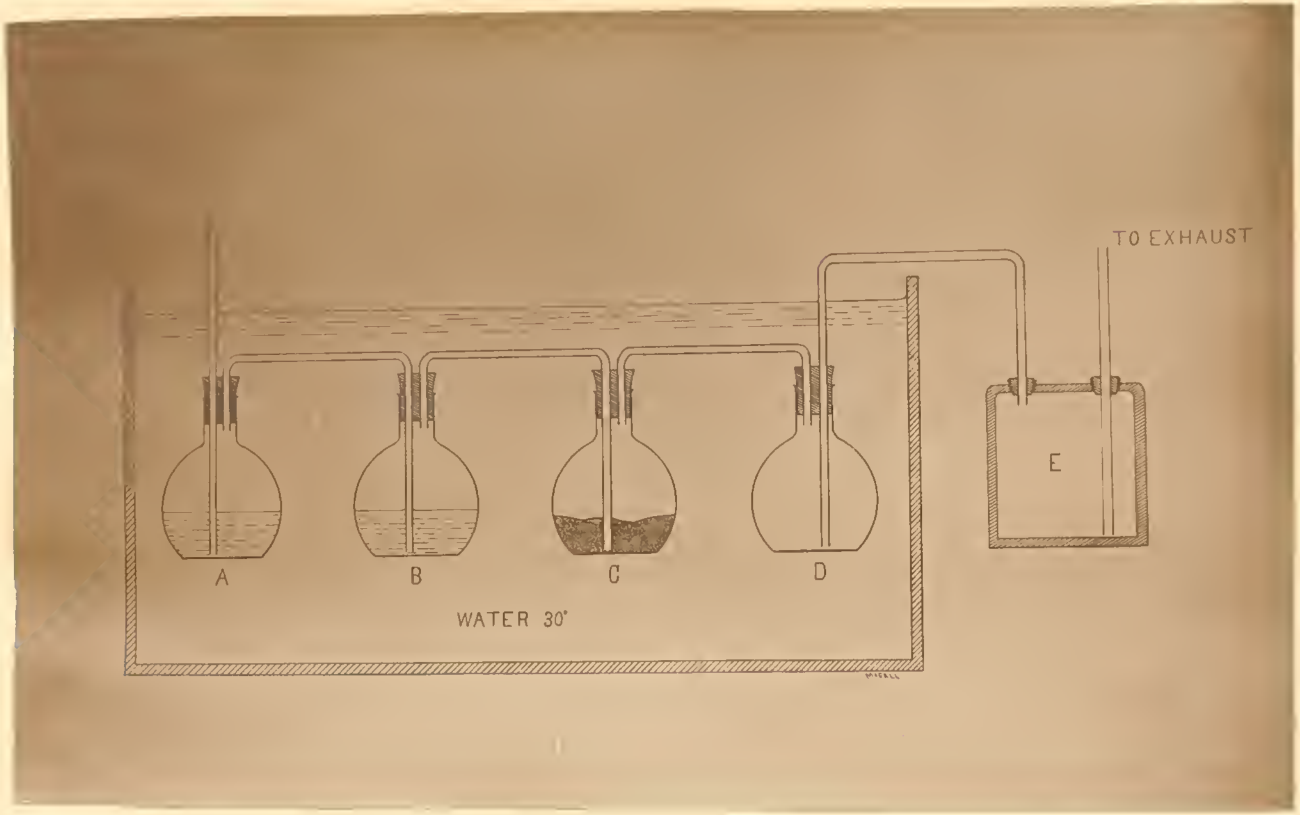


Fig 7 - Apparatus used in investigating the elimination
of water [illegible] by [illegible]

the quartz. In this manner the quartz was always in contact with water vapor at a definite vapor pressure, which was always less than the saturation pressure for pure water at that temperature. Consequently there was no danger of any precipitation taking place, in the ordinary sense of the word. Sir William Thomson has shown that condensation will take place on a concave surface of extremely small radius even when evaporation is taking place from plane or convex surfaces. Since there are a great many concave surfaces formed by particles in contact, this action undoubtedly enters into adsorption phenomena to some extent. When the quartz is stirred, these concave surfaces are destroyed, and new ones formed. It is consequently impossible to say to what extent this phenomenon affects the total amount of adsorption.

In order to bring the quartz into as intimate contact with the water vapor as possible, the apparatus was tilted from time to time so as to bring all portions of the quartz to the surface. The relation between the concentration of the sulphuric acid solutions employed and the vapor pressure is given in the following table taken from the results of Regnault (Landolt and Börnstein, Phys. - Chem.Tab., 2d.Ed.,

p. 65):-

TABLE I.

VAPOR PRESSURE OF SULPHURIC ACID SOLUTIONS -

Solution.	Per cent. H_2SO_4	Vapor press 30° m.m.	Vap.pr.35° m.m.
$H_2SO_4 + 1\ H_2O$	84.5	0.22	0.28
$H_2SO_4 + 3H_2O$	64.5	4.06	5.43
$H_2SO_4 + 5H_2O$	52.1	10.68	14.4
$H_2SO_4 + 9H_2O$	37.7	19.6	26.1
$H_2SO_4 + 17H_2O$	24.3	26.1	34.8

The quartz was thoroughly dried at 110°C before adsorption. After adsorption the quartz was quickly transferred to a wide-mouthed shallow weighing bottle, and weighed. It was then dried in the bottle to constant weight, care being taken to stir the quartz from time to time during the drying. The loss in weight on drying was taken to represent the amount of water adsorbed.

The relation found between the vapor pressure of the water and the amount of water adsorbed is given in the following table.

TABLE II.

ADSORPTION OF WATER VAPOR BY QUARTZ - 30°.

Vapor pressure m.m.	Amt. Quartz gms.	Water adsorbed gms.	Adsorption pr.100 gms
26	52.975	.037	.0698
19.5	54.907	.034	.0619
11.	42.717	.027	.0632
4.	42.820	.014	.0327
0.2	57.088	.007	.0123

It was feared that perhaps in the method just described the quartz was not brought as intimately in contact with the water vapor as was desirable, and the following expedient was next adopted: About fifteen grams of dry quartz were placed in the bottom of a large heavy test-tube, as shown in Figure 5. Above this quartz a smaller test-tube was suspended which was about half filled with the solution of sulphuric acid. The large tube was then closed with a stopper provided with a glass tube, the stopper sealed over with wax and the pressure within the tube reduced to about 3 cm. of mercury. Five concentrations of sulphuric acid were used and duplicate tubes were prepared. These tubes were then placed in a large tank of water which underwent very slight changes in temperature. By rotating these tubes on their axes inclined at an angle of about 45° with the vertical, practically all the quartz could be brought to the surface. These tubes were allowed to stand for about one week with an occasional stirring of the quartz and were then opened, the quartz rapidly transferred to weighing bottles, weighed, and dried at 110° to constant weight, the difference in weight being taken to represent the amount of water adsorbed.

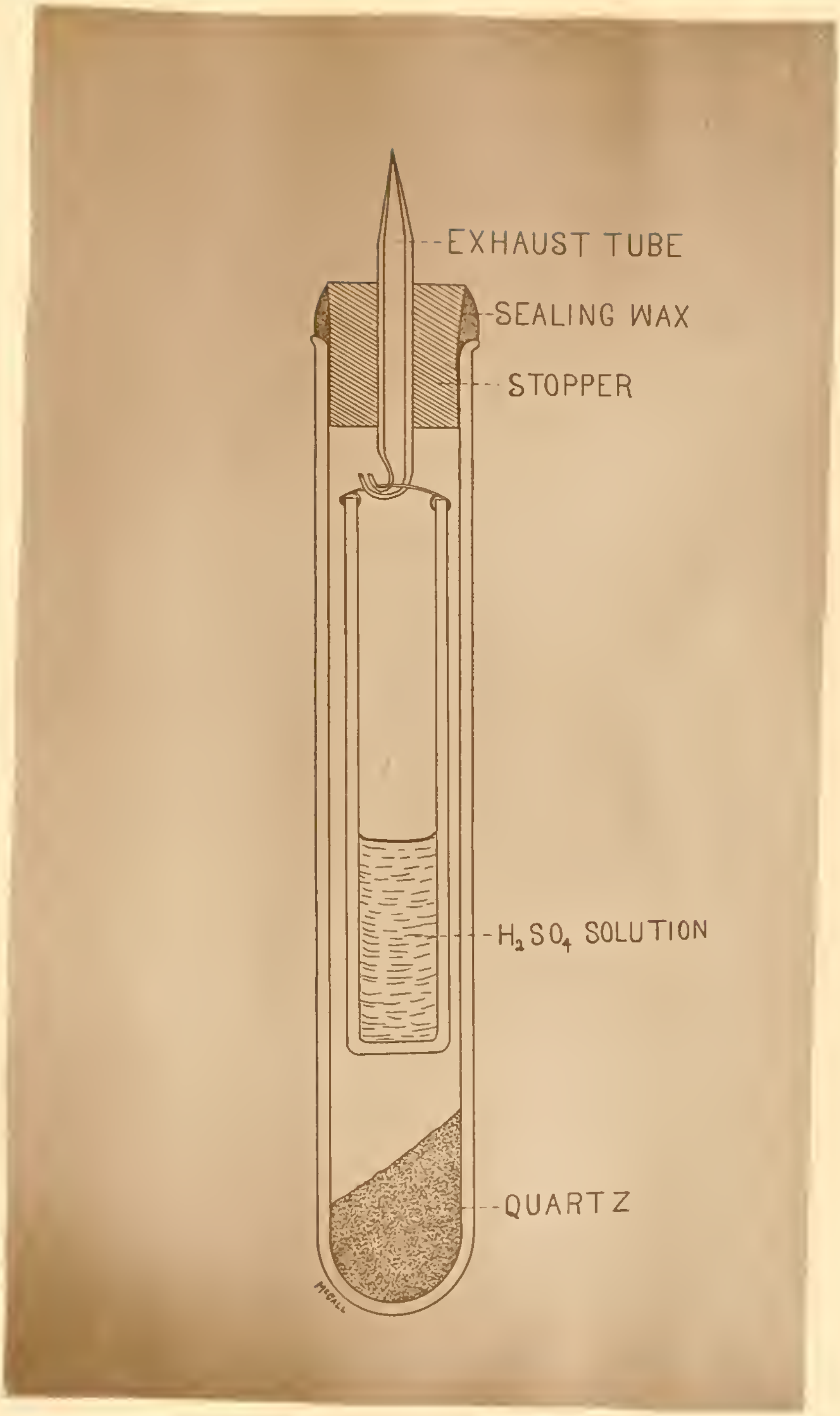


Fig 5 Reaction tube [illegible] of [illegible]
[illegible] of [illegible]

The results obtained are given in the following table:

TABLE 3.

ADSORPTION OF WATER VAPOR BY QUARTZ - 22°.

(Sealed Tube Method)

Vapor pressure (22) m.m.	Wt. Quartz gms.	Water adsorbed	Adsorption pr.100 grms.Quartz
16.3	14.784	.010	.068
	14.545	.008	.055
12.2	14.849	.008	.054
	14.959	.011	.073
6.6	13.761	.005	.036
	14.783	.006	.040
2.5	14.170	.005	.035
	14.837	.003	.020
0.16	14.701	.003	.020
	14.948	.004	.026

In order to avoid all uncertainty regarding intimate contact between the quartz and the water vapor, a third method was devised in which the quartz was constantly stirred while in the presence of the water vapor. The apparatus used for this purpose is shown in Figure 6, which was substituted for flask C in the apparatus shown in Figure 4. The water vapor from the train of bottles passes in through one of the side tubes, then over the quartz, and out through the other side tube to the pump. The quartz in the meantime is constantly stirred by means of the stirring apparatus shown in the figure. The blades of the stirrer were so arranged that the quartz was constantly lifted from the floor of the chamber and fell over and behind the blades as they revolved. The stirrer was driven at a velocity of six or eight revolutions a second by means of a small electric motor attached directly to the shaft, the speed being cut down by a suitable series resistance. It was of course necessary to have the whole apparatus immersed in water in order to maintain a constant temperature so that danger of condensation might be eliminated. Consequently, it was necessary that the shaft be provided with a water-tight seal where it passed through the cover of the chamber containing the quartz.

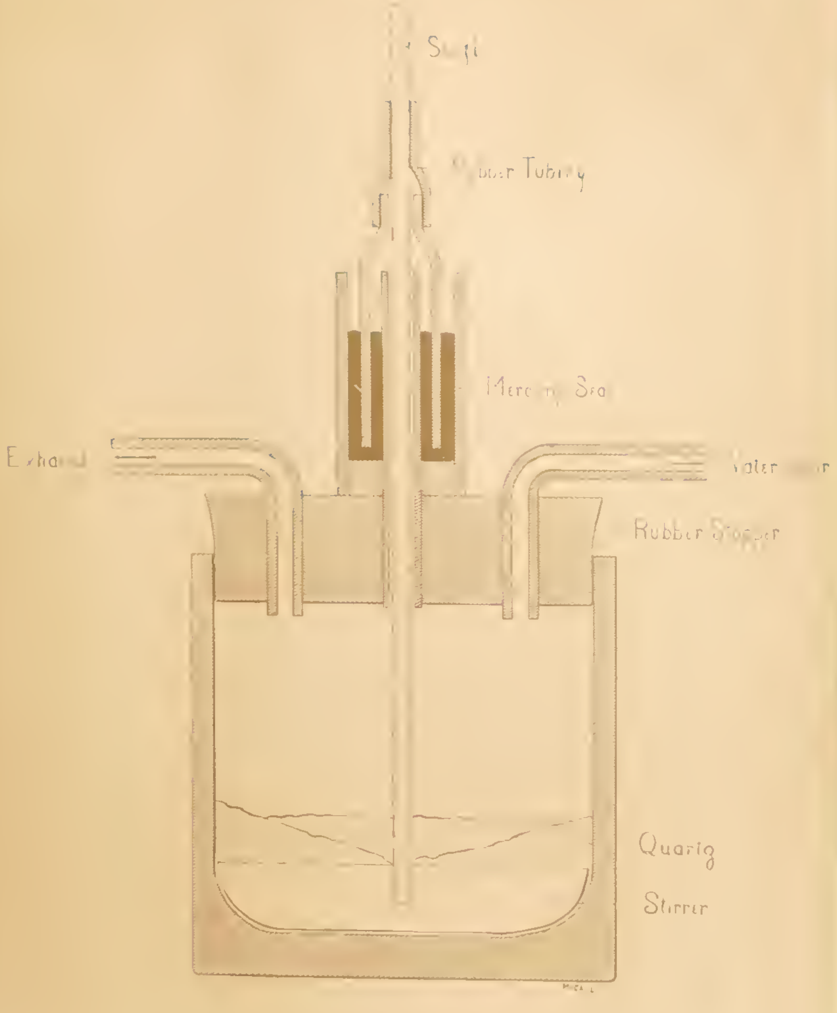


Fig. 6 - Container [illegible]
[illegible]

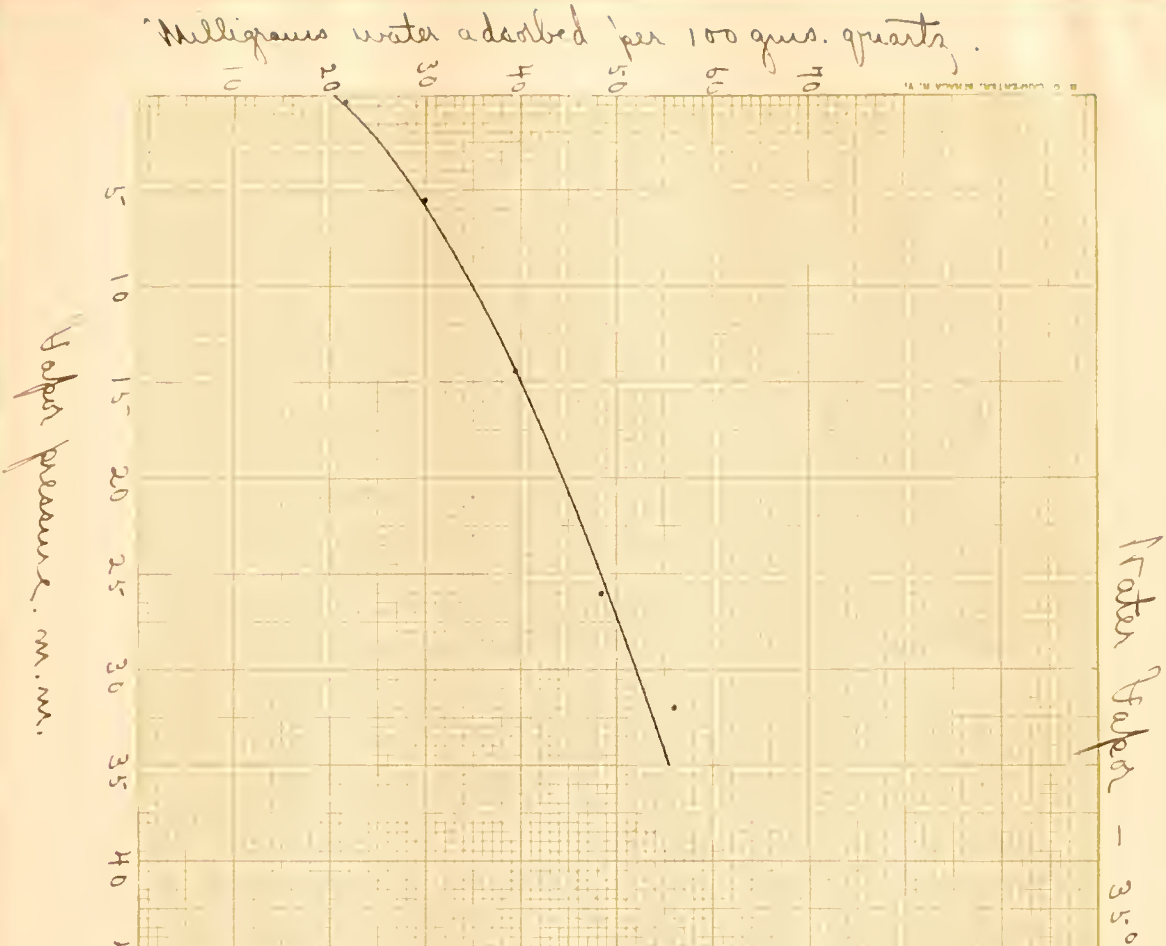
This was secured by a mercury seal as shown in the figure. A glass tube of an internal diameter slightly larger than the shaft passed through the centre of the rubber stopper closing the chamber containing the quartz, and projected about 4 cm. above its upper surface. To this tube was fitted another glass tube of much larger diameter by means of a short rubber stopper at the base. A third tube of a diameter intermediate between the first two tubes was drawn down at one end to a diameter slightly larger than that of the shaft. It was then fastened to the shaft by rubber tubing with its larger end downward in the position shown in the figure, and the outer cup was then half filled with mercury. This arrangement permitted a perfectly free rotation of the shaft and at the same time made a water tight seal so long as the difference in pressure between the inside and outside of the quartz chamber was not sufficient to force some mercury over the top of the inner tube.

The results obtained by means of this apparatus are given in Table IV. and illustrated graphically in the accompanying figure:-

TABLE IV.

ADSORPTION OF WATER VAPOR BY QUARTZ - 35°.

Vapor pressure m.m.	Amt Quartz gms.	Water adsorbed gms.	Adsorption per 100 gms.
32	39.405	.022	.0558
26	39.182	.019	.0485
14.5	35.507	.014	.0394
5.5	40.431	.012	.0297
.2	37.871	.008	.0214


Milligrams water adsorbed per 100 gms. quartz.
10
20
30
40
50
60
70
Vapor pressure. m.m.
5
10
15
20
25
30
35
40
45
50
Water Vapor - 35° C.

ADSORPTION OF CARBON DIOXIDE BY QUARTZ.

Plan of the Experiments.

It is well known that the hydrates and normal carbonates of the alkaline metals have the power to unite with carbon dioxide, forming acid carbonates. This principle has been made use of in the present experiments to determine the amount of adsorbed carbon dioxide, the adsorbing material being directly treated with a dilute aqueous solution of sodium hydrate or carbonate of known concentration - a method which does not appear to have been heretofore employed in adsorption determinations.

A known weight of the finely divided solid upon which the carbon dioxide is adsorbed, is shaken in a tightly stoppered bottle with a measured quantity of the solution, whose concentration and composition has been previously determined. The carbon dioxide adsorbed on the surface of the solid now gradually passes into solution and reacts with the sodium hydrate. After continuous shaking for about thirty min-

utes a quantity of the solution is removed from contact with the solid and again titrated with a standard acid.

There exists in the potassium hydroxide solution, after shaking with a solid upon which carbon dioxide was adsorbed, potassium hydroxide, potassium carbonate, and potassium acid carbonate, all more or less dissociated. This supposes that the amount of solution was in excess of that necessary for complete reaction with the carbon dioxide. Experiment has shown that in the presence of an excess of potassium hydroxide the amount of free carbon dioxide is negligible, - a fact upon which the prevailing method of estimating carbon dioxide depends.

If now the solution is titrated with a solution of a dilute acid - say hydrochloric acid - using phenol phthalein as an indicator, which is sensitive to carbonic acid, the following reactions take place:

$$KOH + HCL = KCl + H_2O$$

$$K_2CO_3 + HCl = KHCO_3 + KCl$$

We see from these two reactions that the final result of the titration, using phenol phthalein as an indicator, is the same as if no potassium carbonate had been formed, since one of the two potassium ions which are combined as potassi-

um carbonate behaves on titration as if it were still combined with hydroxyl. The total amount of carbon dioxide is consequently represented by the amount of acid potassium carbonate in the solution. This is determined by adding a second indicator (methyl orange), which is not sensitive to carbonic acid, to the solution already titrated with phenol phthalëin as an indicator, and proceeding with the titration until the color change in this indicator, due to excess of acid, is barely discernible. The amount of acid added during the second titration is proportional to the amount of combined carbon dioxide in the solution, the reaction proceeding as follows:

$$KHCO_3 + HCl = KCl + CO_2 + H_2O$$

The amount of the solution of standard acid used during the first part of the titration with phenol phthalëin as an indicator is consequently unimportant, unless the adsorption of the dissolved substance is also under investigation. Care must, however, be taken not to run in the acid too rapidly, and the end of the reaction must of course be determined as sharply as possible; since it forms the basis for the second titration in which methyl orange is used. Other acids and indicators for the estimation of carbonates and

acid carbonates are favored by some investigators. A discussion of the estimation of these acids will be found in a paper by Cameron(*)

In some of the adsorption determinations given in this paper, a solution of sodium carbonate was used instead of potassium hydroxide. An investigation of the equilibrium of carbonates and hydrogen carbonates in the presence of carbon dioxide by Dr. F. K. Cameron and myself, has shown that this procedure was justifiable; since for dilute solutions by far the greater amount of the base is combined as acid carbonate, and, consequently, in a dilute solution of sodium carbonate reaction with carbon diozide readily takes place. The system is, however, in equilibrium with a slight amount of uncombined carbon dioxide and, while this is no doubt exceedingly small, it seems preferable to use the hydroxide; for in this system the amount of uncombined carbon dioxide is apparently negligible.

Adsorption of Carbon Dioxide by Quartz Sand.

The first experiments regarding the adsorption of

(*) Am. Chem. Journal, 1900

carbon dioxide were made with quartz sea sand as the adsorbing material. This sand was perfectly clean and white in appearance and about a year previously had been thoroughly washed with distilled water to remove as much of the soluble matter present as possible. After washing, it was dried at room temperature and has since been kept in a considerable quantity in a loosely stoppered jar.

Samples of 100 grams of this sand were placed in 250 c.c. shaking bottles, together with 100 c.c. of approximately tenth normal sodium carbonate, and shaken for definite periods of time. This was done, not so much for the purpose of finding the time necessary for equilibrium to be established between the carbon dioxide and the sodium carbonate, but more particularly to find the time required for the sodium carbonate solution to attain equilibrium with the quartz sand, since this solution also undergoes adsorption when brought in contact with the solid. We are in such cases, therefore, really making a double determination: First, the amount of carbon dioxide already adsorbed on the solid, and second, the amount of sodium carbonate which is adsorbed from the solution. It is, however, with the adsorption of carbon dioxide that we are here chiefly concerned.

In Table V. will be found the results obtained for the adsorption of carbon dioxide by quartz, the sodium carbonate solution having been shaken with the quartz for periods varying from five minutes to seven days. The titrations were made in each case upon aliquot parts of the clear supernatant solution.

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TABLE V.

ADSORPTION OF CARBON DIOXIDE BY QUARTZ SAND.

How treated	Amount c.c.	Amount HCl required Phenol phthalein	Methyl orange	Total
Stock Na_2CO_3 Solution	10	4.6	4.55	9.15
	10	4.55	4.58	9.13
Shaken 5 minutes	10	4.42	4.6	9.02
	10	4.45	4.55	9.0
Shaken 1 hour	10	4.40	4.65	9.05
	10	4.40	4.7	9.1
Shaken 3 hours	10	4.45	4.65	9.1
	10	4.40	4.7	9.1
Shaken 7 days	10	4.40	4.70	9.1
	10	4.36	4.66	9.02
Mean before Adsorption	10	4.57	4.57	9.14
Mean after Adsorption	10	4.41	4.65	9.06

The first column of the table gives the time which the sample was shaken; the second column gives the amount of the sodium carbonate solution used in each titration; the third column states the number of cubic centimeters of a one-tenth normal acid required to neutralize the solution of sodium carbonate, using phenol phthalëin as an indicator; the fourth column gives the additional amount of the acid which is necessary to add to the same portion of solution when methyl orange is introduced as an indicator after the completion of the reaction as indicated by phenol phthalëin; the last column gives the total amount of acid required to completely neutralize the sodium carbonate solution.

At the top of the table will be found the composition of the sodium carbonate solution before being added to the quartz sand. The two lower lines of the table give the mean of the values obtained before and after being shaken with the quartz sand.

It will be noticed that the mean of the determinations before adsorption show that equal amounts of acid were used with each indicator, that is, that no acid sodium carbonate was present in the solution before adding the quartz. The subsequent formation of acid sodium carbonate can only take

place in the presence of carbon dioxide, and the only source of carbon dioxide is that adsorbed on the surface of the quartz. Consequently, the difference in the amount of acid required with each indicator after the addition of the quartz gives the amount of acid sodium carbonate found and consequently the amount of carbon dioxide supplied.

The amount of acid sodium carbonate formed is equivalent to 4.65 - 4.41 = 0.24 cc. of a tenth normal acid for each 10 cc. of solution, or 2.4 cc. for the 100 grams of quartz. The weight of acid sodium carbonate in 2.4 cc. of a tenth-normal solution is 0.0202 grams. Of this amount 0.0106 grams is carbon dioxide. In 100 cc. of the quartz sand(dry) the interstitial space is about 45 cc. The amount of carbon dioxide in atmospheric air is, according to Mendeleeff* about 3 parts in 10,000 by volume. The mass of carbon dioxide at 0°C., and 760 m.m. pressure is 1.974 grams per litre. Therefore the mass of carbon dioxide per litre of atmospheric air under standard conditions is 0.00059 grams. The 45cc interstitial space would therefore, if filled with atmospheric air, contain 0.000026 grams of carbon dioxide. But if we

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(*) Principles of Chemistry, Vol. I., p.228.

consider the adsorbed carbon dioxide as being free in the interstitial space the amount of carbon dioxide present would be, as we have seen, 0.0106 grams. Therefore, the amount of carbon dioxide present through adsorption in this relatively coarse material is about 400 times the amount which would be present if the interstitial spaces were filled with atmospheric air and no adsorption had taken place. This fact can but serve to emphasize the importance of adsorption in all systems where a reaction with carbon dioxide is possible.

The question at once arises: Is the reaction which was apparently observed with carbon dioxide due entirely to carbon dioxide? May not the sodium carbonate react with the quartz to form acid sodium carbonate and acid sodium silicate? The latter substance reacts like acid sodium carbonate on titration, so that no distinction could be made by this means.

To settle this question a number of determinations were made in various ways, all of which appear to establish conclusively that no reaction between the sodium carbonate and the quartz takes place to an appreciable extent during the time employed in the experiments. On referring to Table V. it will be seen that the time of contact between the

sodium carbonate and the quartz varied from five minutes to seven days. If the sodium carbonate reacted with the quartz the amounts of the products of the reaction should be a function of the time, probably directly proportional to the time, since the velocity of the reaction is unquestionably very small. Yet it will be seen in referring to Table V. that the apparent amount of acid sodium carbonate formed was no greater at the end of the longer periods. From this we are justified in concluding that the observed inversion of the sodium carbonate is not due to a reaction with the quartz, but with the carbon dioxide adsorbed on the surface of the quartz.

This point was also tested in another way. Calcium carbonate was used as the adsorbing material, and the adsorption of sodium carbonate determined. Since these substances have a common ion, no reaction is supposed to take place between the two substances. Yet, here again, the formation of a small amount of acid sodium carbonate was noted, indicating the presence of adsorbed carbon dioxide.

Adsorption of Carbon Dioxide by Powdered Quartz.

Further data on the adsorption of carbon dioxide at its partial atmospheric pressure may be found in Tables VI., VII., and VIII. in connection with the discussion of the adsorption of sodium carbonate.

ADSORPTION OF SALTS IN AQUEOUS SOLUTION BY QUARTZ.

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Preliminary Work.

In the preliminary work on this subject, a white quartz sea sand was used as the adsorbing material, and the adsorption of sodium carbonate was investigated. One hundred gram portions of the carefully washed sand were shaken with 100 cc of a tenth normal solution of sodium carbonate, for different periods of time. The results obtained are given in Table V, the difference in the total amount before and after adsorption giving the amount adsorbed from each 100 cc. of the solution. The total adsorption of the 100 grams of quartz sand is, therefore, ten times this amount, or is equal to (9.14-9.06) 10 = 0.8 c.c. of $\frac{N}{10}$ Na_2CO_3, or about 4 milligrams of the salt. From these figures, it is evident that a little less than one per cent. of the total salt in the solution was removed.

The adsorption of sodium carbonate from hundredth normal solutions by quartz sand was also studied. The results are given in Table VI.

TABLE VI.

Adsorption of N/100 Na_2CO_3 by quartz sand.

		Amount $\frac{N}{100}$ HCl required.		
How treated.	Amount cc.	Phenol phthalëin.	Methyl orange.	Total.
Stock Na_2CO_3 Solution	10	4.15	5.40	9.55
	10	4.20	5.25	9.45
Shaken 30 minutes	10	3.25	6.10	9.35
	10	3.30	6.	9.30
Shaken 7 days	10	3.60	5.70	9.30
	10	3.65	5.75	9.40
Mean before adsorption	10	4.17	5.32	9.50
Mean after adsorption	10	3.45	5.90	9.34

The adsorption in the case of the N/100 Na_2CO_3 in contact with 1 gram of quartz per cubic centimeter appears to be about 2 per cent., or twice that obtained with the N/10 solution. The actual amount of salt adsorbed is, however, one one fifth that removed from solution in the greater

concentration. The amount of acid sodium carbonate formed represents about 15 per cent. of the total sodium present. Nearly the same amount originally existed in the solution in this form, as shown by the titrations on the stock solution, so that the total amount of acid sodium carbonate present at the close of the experiment constituted about 30 per cent of the total sodium present.

The adsorption of sodium carbonate by powdered quartz was next studied, with the following results:

TABLE VII.

Adsorption of N/10 sodium carbonate by powdered quartz.

How treated.	Amount cc	Amount N/10 HCl required. Phenol phthalein.	Methyl orange.	Total.
Stock N/10 Na_2CO_3 Solution	10	4.6	4.6	9.2
	10	4.6	4.68	9.28
	10	4.65	4.60	9.25
Shaken 30 minutes with quartz	10	4.20	4.8	9.00
	10	4.20	4.83	9.03
	10	4.23	4.80	9.10
Mean before adsorption	10	4.62	4.63	9.24
Mean after adsorption	10	4.21	4.81	9.04

TABLE VIII.

Adsorption of N/100 sodium carbonate by powdered quartz.

		Amount N/100 HCl required.		
How treated.	Amount. cc	Phenol phthalein.	Methyl orange.	Total.
Stock N/100 Na_2CO_3 Solution	10	4.15	5.40	9.55
	10	4.20	5.25	9.45
Shaken 30 minutes with quartz	10	1.20	7.55	8.75
	10	1.30	7.48	8.78
Mean before adsorption	10	4.17	5.32	9.50
Mean after adsorption	10	1.25	7.51	8.76

From Table VII it will be seen that 10 cc. of the tenth normal solution of sodium carbonate were equivalent to 9.24 cc. of the standard acid before shaking with the ground quartz, while 9.04 cc. were required after adsorption had taken place; consequently, about 2 per cent. of the sodium carbonate had been adsorbed. Since the original solution was approximately tenth-normal and the ratio between the adsorbing substance and solution was 1 gram per cubic centimeter, it follows that .000106 gram, or approximately one tenth of a milligram, of salt per gram of quartz had been

adsorbed under the conditions given above.

Relation between Quantity of Sodium Carbonate Adsorbed and Surface Area of Adsorbing Material.

The determination of the relation between the amount of salt adsorbed and the area of the adsorbing surface obviously necessitates some means of measuring the surface area of the adsorbing material. No very satisfactory method for such measurements is known. Gore and others have attacked the problem by measuring the rise in temperature occasioned by moistening the pulverized body with water, but this gives only relative results. Mitscherlich[1] has endeavored to standardize this method by comparing his results with the surface area computed from mechanical analysis. No measurements with a known surface area seem to have been made by any of these investigators.

Recourse to the results obtained by mechanical analysis is consequently necessary for the determination of the

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[1] Inaugural Dissertation. Kiel, 1898. Jour. fur Landwirtshaft, 1898, S. 255.
Jour. fur Landwirtshaft, 1900, S. 71.

amount of surface. In the following calculations the particles have been considered cubical in form rather than spherical, which is the form ordinarily adopted. The reason for this change is that a calculation on the basis of a cube seems much more likely to give results more closely approximating the actual surface area of a particle, which is generally quite irregular in form, whereas the spherical grains offers the minimum surface possible for the given mass.

The mean value of the limits for any group has been taken as the basis of computation. This has been assumed equal to the longest diagonal of the cube; that is, the line from one corner of the lower face to the diagonally opposite corner of the upper face. It is evident that if the length of the edge of the cube be $\underline{a}$, the length of this diagonal is $\underline{a}\sqrt{3}$. On this basis the following table has been computed, giving the surface area per gram for each separation.

TABLE IX.

Surface area of separations as grouped in mechanical analyses. (Computations based on quartz sp. gr. 2.65.)

Grades m.m.	Mean diameter m.m.	Length of edge of cubical grain m.m.	No. of grains per gram.	Surface area per gram sq.cm.
1 2.- 1.	1.5	.8662	580	26.14
2 1.-.5	.75	.4331	4,645	52.3
3 .5 -.25	.375	.2165	37,180	104.6
4 .25-.1	.175	.1010	365,900	223.9
5 .1 -.05	.075	.0433	4,645,000	522.4
6 .05-.01	.03	.0173	72,610,000	1307.
7 .01-.005	.0075	.0043	4,645,000,000	5224.
8 .005-.0	.0025	.0014	125,500,000,000	9963

Applying the data given in Table IX to the mechanical analysis of the quartz sand (p. 17) it will be seen that

this material presents approximately 145 sq. cm. of surface per gram. From Table V it will be seen that (9.14-9.06) /914 or 8/914 of the salt in 100 cc. of tenth normal sodium carbonate solution was adsorbed by 100 grams of the sand. This corresponds to an adsorption of 4.6 mg. of salt by 14500 sq. cm. of surface from a tenth-normal solution, or 1 milligram to 3000 sq. cm. of surface.

A similar computation for the powdered quartz (p. 10) shows it to present a surface area of 1000 sq. cm. per gram. The salt adsorbed by 100 grams of this material was 20/924 of the amount present in 100 cc. of a tenth normal solution of sodium carbonate or 0.0114 gram. This is equivalent to 1 milligram of salt per 9000 sq. cm.

Measuring Adsorption by Ostwald and Kelberin's Method.

The method of measuring adsorption just described contains an element of uncertainty owing to the fact that the amount of surface exposed in the various samples of quartz may not be the same. For this reason it was decided to try the method of Ostwald and Kelberin, in which the same

sample of quartz would be employed throughout the series of determinations for any one salt. Their method as stated above consists in bringing a weighed amount of charcoal into equilibrium with a known volume of a concentrated solution of the substance under investigation, then removing a definite volume of the solution for analysis and replacing it with an equal volume of water. Equilibrium was then again established between the adsorbing material and the more dilute solution and the process repeated as before.

Two 50 cc. pipettes were carefully calibrated, one to receive 50 cc. and the other to deliver an equal volume under standard conditions. They were then compared with each other and the cumulative error introduced by first delivering 50 cc. into a weighing bottle containing a little water, and then removing the same amount with the receiving pipette, amounted to less than 0.1 cc. at the end of five cycles. Two-normal solutions of sodium, potassium, ammonium, calcium and magnesium chlorides were prepared, and 100 cc. of each solution were added by means of the delivering pipette to corresponding 100 gram portions of washed quartz

in flint-glass bottles of about 250 cc. capacity. These bottles were closed with soft rubber stoppers, which were forced tightly into place and then wired to prevent any possible leakage.

The bottles were then placed in the reciprocating mechanical shaker shown in Figure 1, and allowed to shake for several days. 50 cc. of each solution were then withdrawn with the receiving pipette and a corresponding amount of water added, after which the process just outlined was repeated. The solution withdrawn was either made up to a greater volume for convenience in titrating, or portions were titrated directly, depending on the concentration.

If adsorption had taken place to an appreciable extent, the concentration of the nth dilution should be more than one-half that of the n-1 dilution. The extremely small change, however, in the concentration of the original solutions after shaking with the quartz gave rise to doubts as to whether any differences could be observed, and this was verified when the subsequent dilutions were examined, the effect of adsorption being so small as to be masked by the

experimental errors which are necessarily cumulative in this method.

Another feature which is liable to lead to erroneous results is the change in volume due to the dilution of the solutions, which, if uncorrected, would give results apparently indicating adsorption. The method is not therefore adapted to systems in which the adsorption is comparatively small, and,after a thorough trial and considerable loss of time, was finally abandoned altogether.

Method Finally Employed in Measuring Adsorption in Aqueous Solutions.

The method next adopted and the one employed in practically all the measurements was the same as that used in the preliminary experiments. A series of solutions of each substance under investigation was prepared, and the concentration of each solution before and after adsorption was determined directly by titration. One hundred and fifty cubic centimeters of solution were for each 100 gms. of quartz. The solution and powdered quartz were always shaken together for at least thirty hours in the mechanical

shaker shown in Figure 1, which insured constant and thorough contact between the solution and the solid. No special effort was made to keep the temperature constant in this part of the work, the systems being subject to the fluctuations of room temperature, which averaged about 22° C. the extreme variation being from 18° to 30° C.

Description of Results.

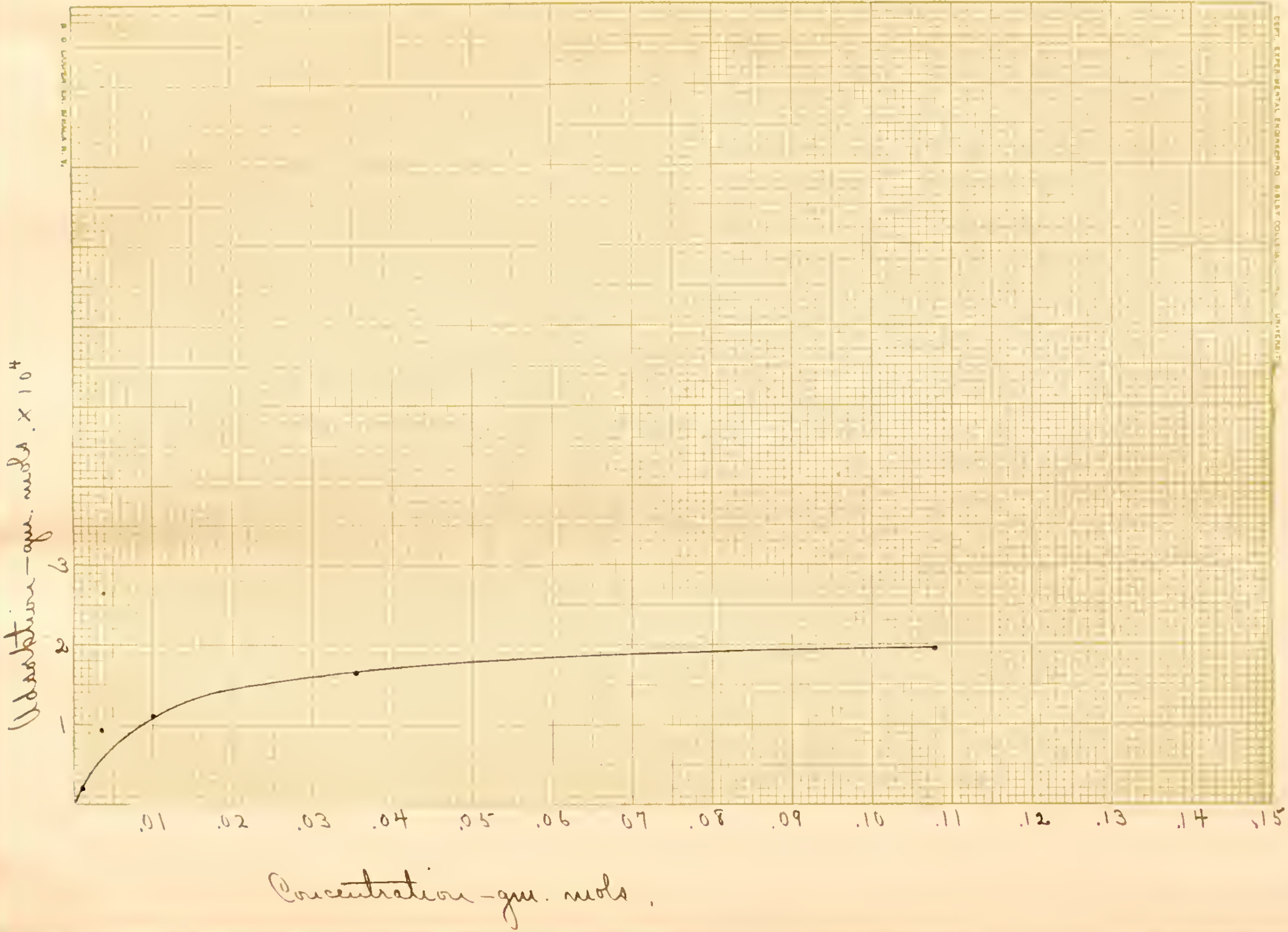
In the following tables the first column gives the concentration of the solution after adsorption in gram-molecules per liter; that is, the portion of a molecular weight of the salt in grams in one liter. In the case of the carbonates the molecular weight was divided by 2. The second column gives the amount of solution which was used in each titration. The third column gives the titrating reagent employed. The fourth and fifth columns give the amount of the titrating reagent required to neutralize the amounts titrated before adsorption and after adsorption respectively. The sixth column gives the mean difference of these two determinations, while the last column gives

the total adsorption of salt in gram molecules by 100 grams of quartz for that particular concentration. Several titrations of each solution were made, which are grouped together in horizontal rows.

Sodium Carbonate (Na_2CO_3)

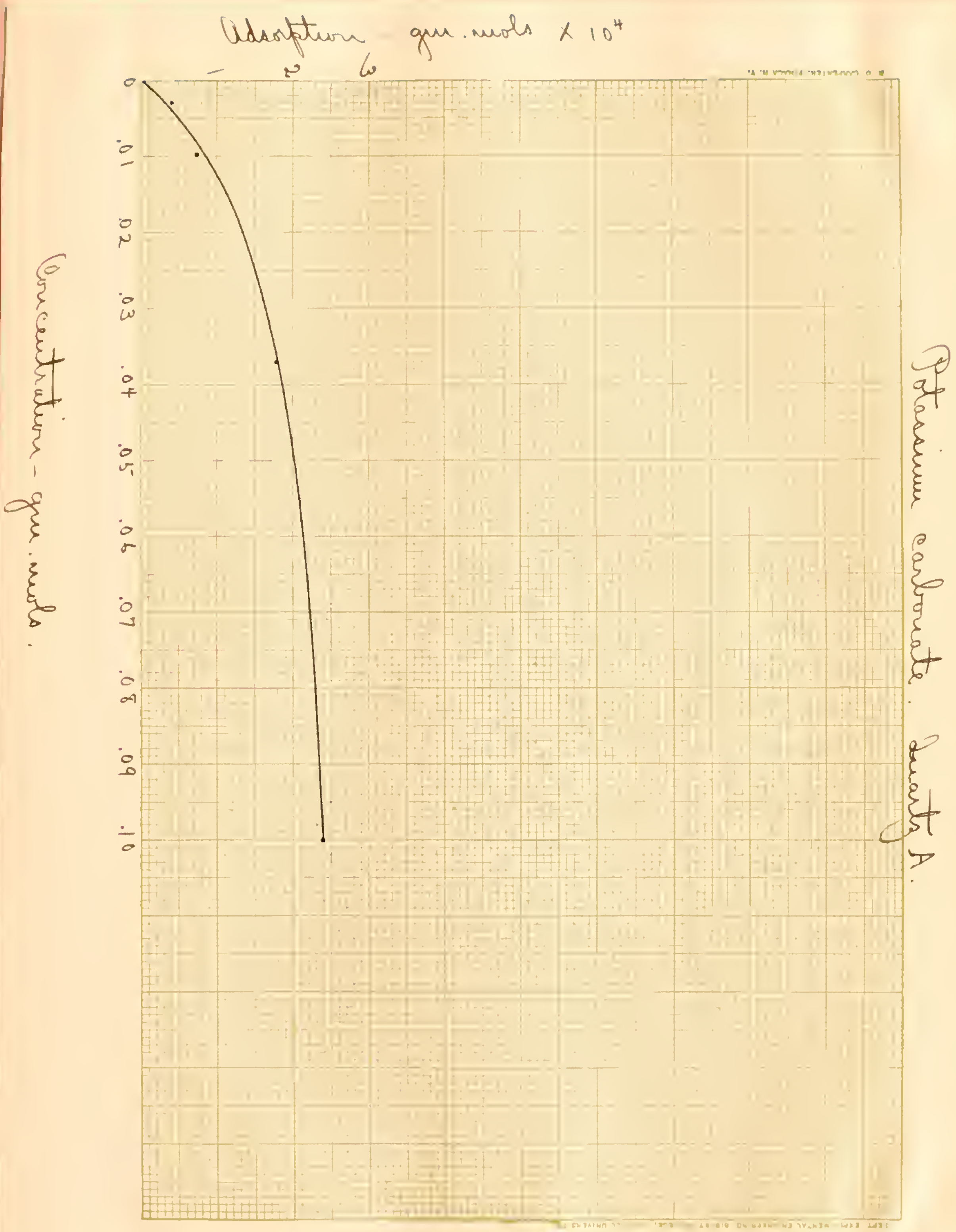
Concentration.	Amount solution titrated.	Titrating reagent.	Amount titrating reagent required		Mean difference.	Total Adsorption.
			Before adsorption.	After adsorption.		
gm.mols.	cc		cc.	cc.	cc.	gm.mols.
0.108	25	N/10 HCl	27.30	26.95	0.325	1.95×10^{-4}
	25		27.30	27.0		
0.0356	25	N/10 HCl	9.20	8.90	0.275	1.65
	25		9.20	8.95		
0.0106	25	N/100 HCl	28.60	26.60	1.89	1.13
	25		28.38	26.60		
0.0032	25	N/100 HCl	9.55	7.92	1.62	0.97
	25		9.55	7.95		
0.0012	25	N/100 HCl	3.32	3.05	.31	0.18
	25		3.34	3.00		
	25		3.32	3.00		
0.0004	25	N/100 HCl	1.10	0.98	.11	0.06
	25		1.09	1.00		
	25		1.11	1.00		

Sodium Carbonate. Quartz A.



Potassium Carbonate (K_2CO_3)

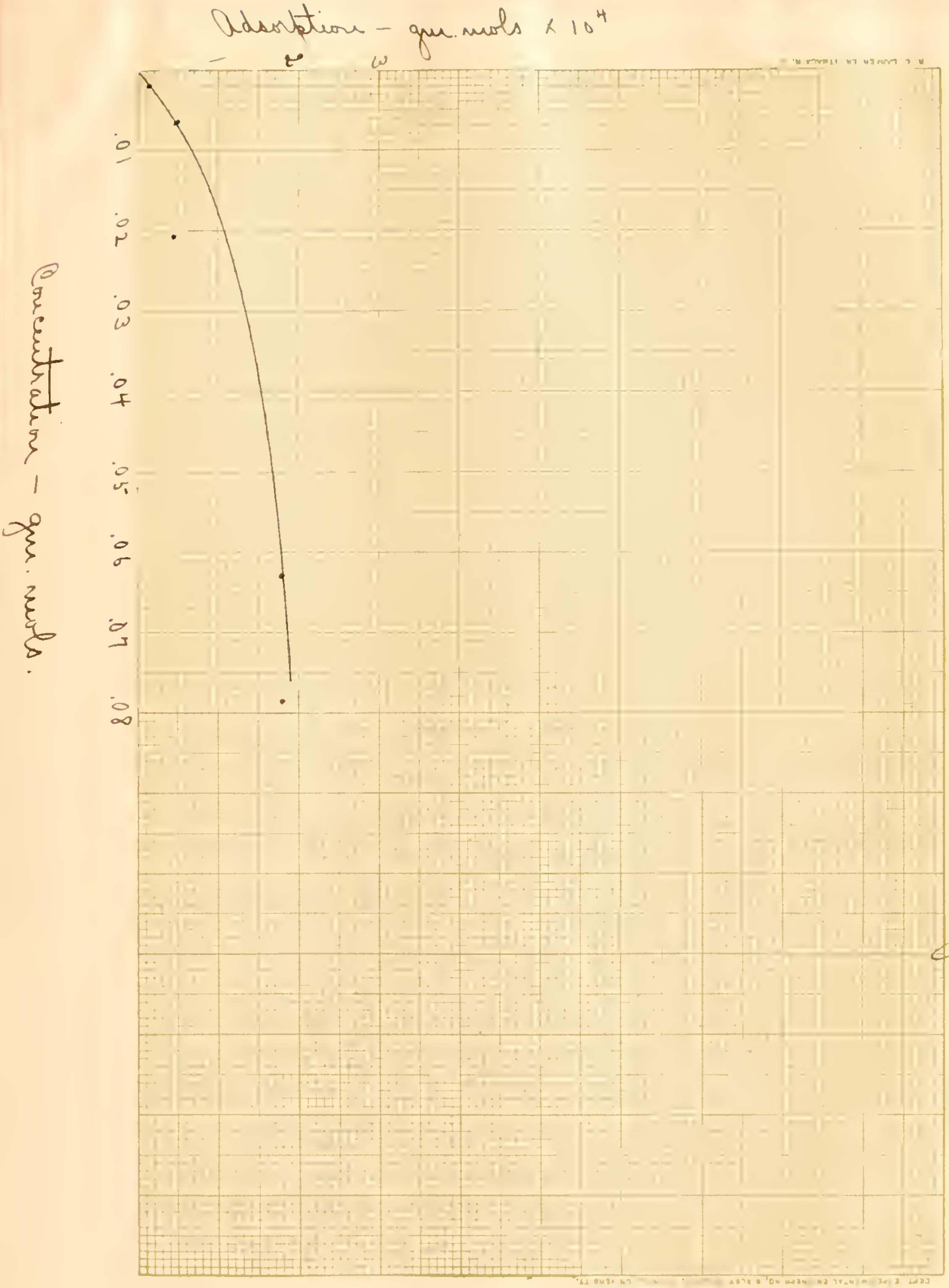
Concentration.	Amt. titrated.	Titrating reagent.	Amt. Titr. Reag. reg.		Mean diff.	Total adsorption.
			Before Ads.	After ads.		
gm.mols.	cc.		cc.	cc.	cc	gm.mols.
0.0910	25	N/10 HCl	23.20	22.75	.40	2.4×10^{-4}
	25		23.10	22.75		
0.0302	25	N/10 HCl	7.80	7.55	.275	1.65
	25		7.85	7.55		
0.0093	25	N/100 HCl	24.48	23.24	1.27	0.76
	25		24.50	23.18		
0.0029	25	N/100 HCl	8.00	7.3	.75	0.45
	25		8.0	7.2		



Potassium carbonate. Quartz A.

Ammonium Carbonate ($(NH_4)_2 CO_3$)

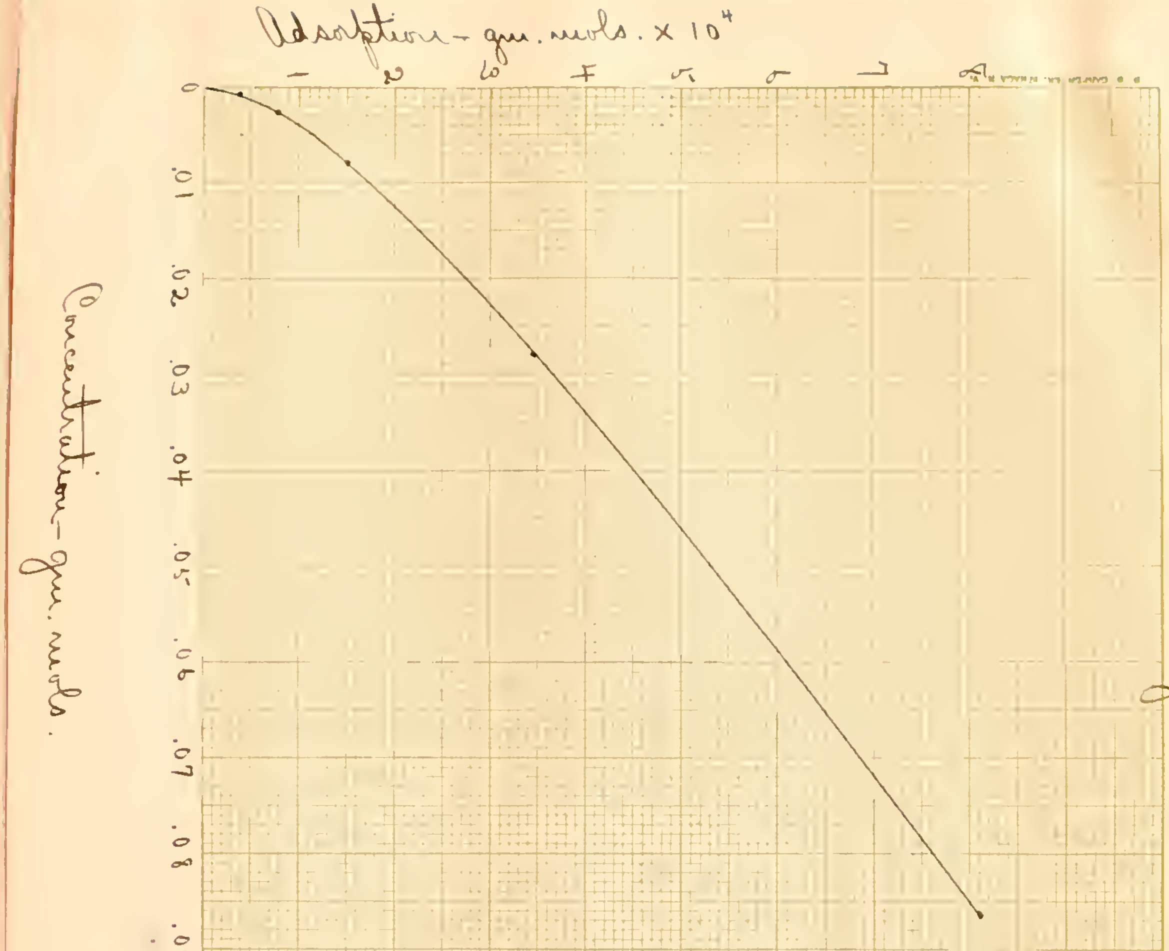
Concentration.	Amt. titrated.	Titrating reagent.	Amt. titr. Bef. ads.	Reag. req. After ads.	Mean difference.	Total adsorption.
gram.mols.	cc.		cc.	cc.	cc.	gm.mols.
.063	25	N/10 HCl	16.0	15.8	0.3	1.8 x 10^{-4}
	25		16.1	15.7		
.0208	25	N/10 HCl	5.3	5.25	0.075	.45
	25		5.3	5.2		
.0065	25	N/100 HCl	17.00	16.15	0.75	.45
	25		16.95	16.30		
.0022	25	N/100 HCl	5.70	5.55	0.15	.09
	25		5.65	5.50		
.0008	25	N/100 HCl	2.05	2.2	-0.12	
	25		2.0	2.25		



Ammonium carbonate. Quartz A

Sodium Hydroxide (NaOH)

Concentration.	Amt. titrated.	Titr. reagent.	Amount titrating reagent required. Before adsorption.	After adsorption.	Mean diff.	Total adsorption.
gm. mols.	cc.		cc.	cc.	cc.	gm.mols.
0.0866	25	N/10 HCl	23.0	21.65	1.35	8.10×10^{-4}
	25		23.0	21.65		
0.028	25	N/10 HCl	7.55	6.95	.575	3.45
			7.55	7.0		
0.0078	25	N/100 HCl	22.05	19.60	2.475	1.48
			22.0	19.50		
0.0026	25	N/100 HCl	7.80	6.55	1.325	.79
			7.90	6.50		
0.0007	25	N/100 HCl	2.45	1.70	.700	.42
	25		2.40	1.75		

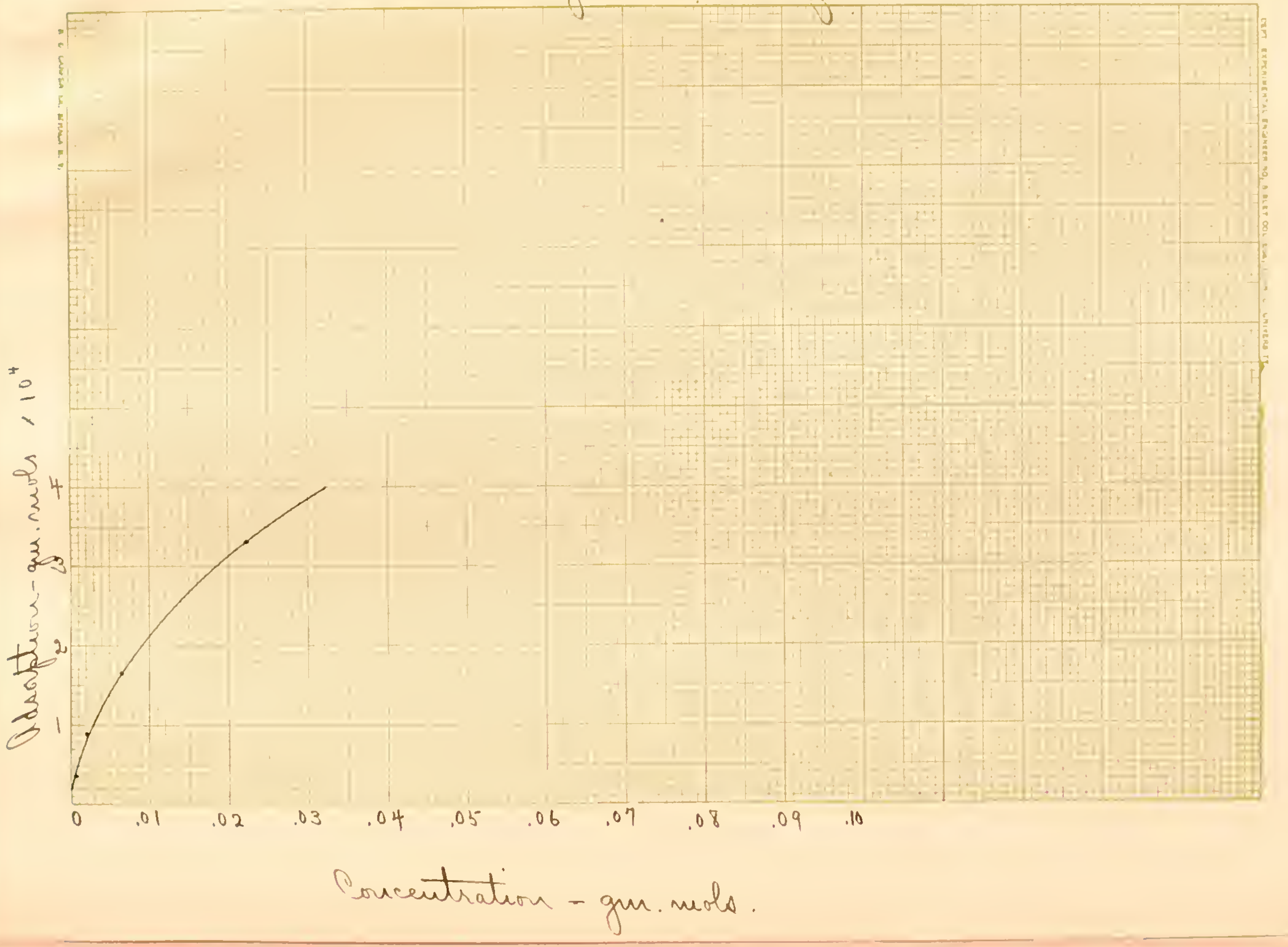


Sodium hydroxide. Quartz A.

Potassium Hydroxide (KOH)

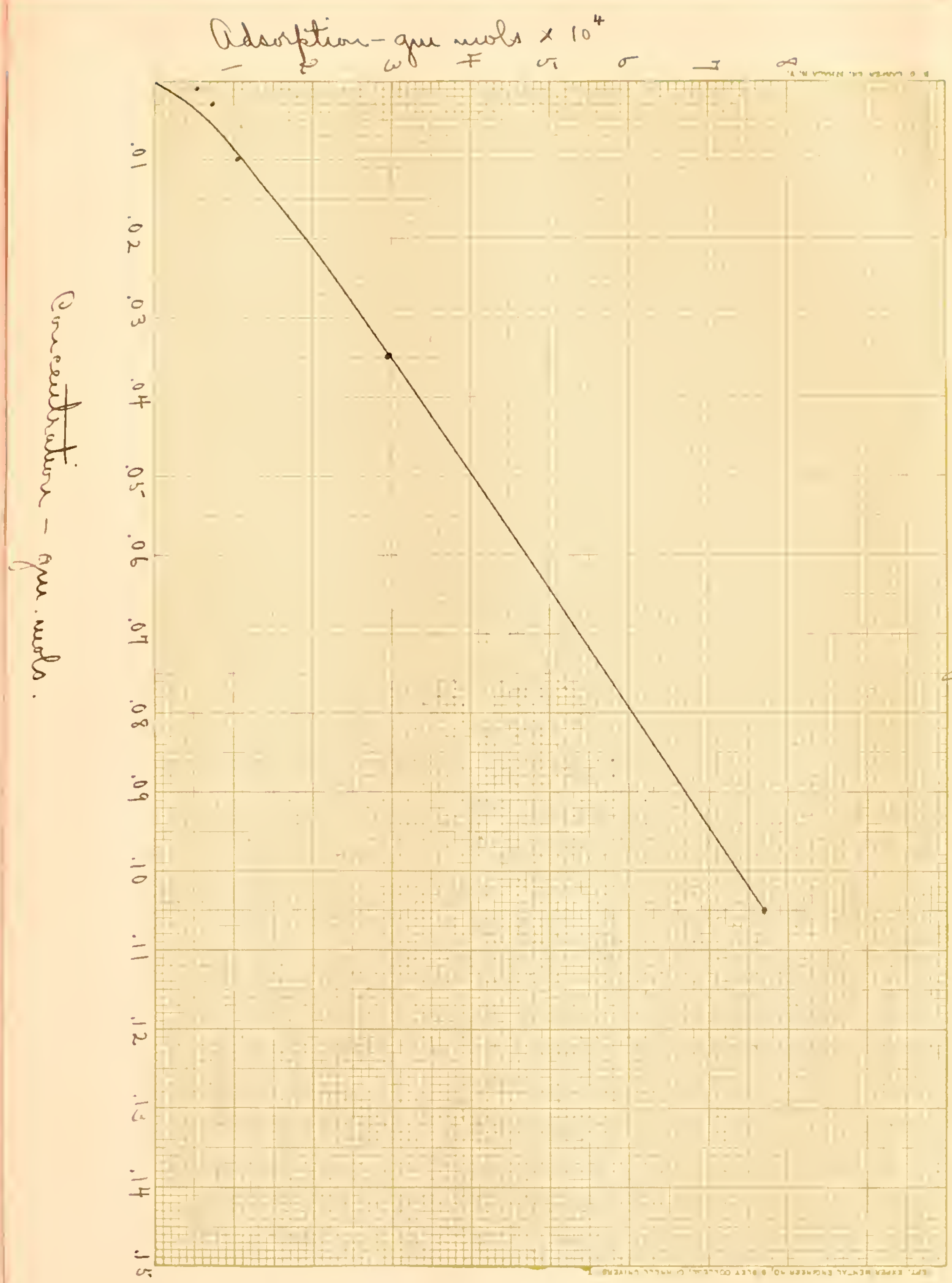
Conc.	Amt. titrated.	Titr. reagent	Amount titrating reagent required Before adsorption.	 After adsorption.	Mean difference.	Total adsorption.
gm.mols.	cc.		cc.	cc.	cc.	gm.mols.
0.0235	25	N/10 HCl	6.10	5.55	.55	3.3×10^{-4}
	25		6.10	5.55		
0.0063	25	N/100 HCl	18.60	15.85	2.725	1.63
	25		18.60	15.90		
0.0021	25	N/100 HCl	6.65	5.20	1.525	0.91
	25		6.70	5.10		
0.0009	25	N/100 HCl	2.15	1.60	.55	0.33
	25		2.10	1.55		

Potassium hydroxide. Quartz A.



Ammonium Hydroxide (NH_4OH)

Concentration.	Amt. titrated.	Titrating reagent.	Amt. titr. reag. required.			
			Before adsorption.	After adsorption.	Mean difference.	Total adsorption.
.1052	25	N/10 HCl	27.50	26.18	1.28	7.68×10^{-4}
	25		27.60	26.33		
	25			26.30		
.0344	25	N/10 HCl	9.10	8.60	.49	2.94
	25		9.10	8.60		
	25			8.62		
.0102	25	N/100 HCl	27.20	25.40	1.73	1.04
	25		27.25	25.40		
	25			25.67		
.0032	25	N/100 HCl	9.40	8.10	1.23	.74
	25		9.35	8.17		
	25			8.16		
.0008	25	N/100 HCl	2.90	1.95	.92	.55
	25		2.90	2.00		
				1.99		



Ammonium hydroxide.

Sodium Chloride (NaCl)

Concentration.	Amount titrated.	Titrating Reagent.	Amount titrating reagent required. Before ads.	After ads.	Mean difference.	Total adsorption.
0.0335	25 cc.	N/10 $AgNO_3$	8.50	8.40	0.085	0.51 x 10^{-4}
			8.45	8.38		
0.00996	25 cc.	N/100 $AgNO_3$	25.35	24.90	0.475	0.275
			25.40	24.90		
0.00347	25 cc.	N/100 $AgNO_3$	8.95	8.65	0.250	0.15
			8.90	8.70		

Ammonium Chloride (NH_4Cl)

Concentration	Amount titrated.	Titrating Reagent.	Amount titrating reagent required.		Mean difference.	Total adsorption.
			Before ads.	After ads.		
0.1003	25 AC.	N/10 $AgNO_3$	25.15	25.10		
			25.10	25.05	0.05	0.30×10^{-4}
0.033	25 cc.	N/10 $AgNO_3$	8.35	8.30	0.075	0.45
			8.40	8.30		
0,00978	25 cc.	N/100 $AgNO_3$	24.55	24.40	0.100	0.06
			24.55	24.50		
0.00343	25 cc.	N/100 $AgNO_3$	8.60	8.55	0,075	0.045
			8.70	8.60		
0.0011	25 cc.	N/100 $AgNO_3$	2.85	2.85	0.0	0.0
			2.75	2.80		

Magnesium Chloride ($MgCl_2$)

Concentration.	Amount titrated.	Titrating reagent.	Before adsorption.	After adsorption.	Mean difference.
gm.mols.	cc.		cc.	cc.	cc.
.096	25	N/10 $AgNO_3$	24.05	24.00	0
	25		24.0	24.05	
	25		24.05	24.05	
	25		24.0	24.0	
.032	25	N/10 $AgNO_3$	8.10	8.1	
	25		8.05	8.10	0
	25		8.05	8.05	
	25		8.05	8.05	
.0097	25	N/100 $AgNO_3$	24.2	24.25	
	25		24.25	24.2	.02
	25		24.4	24.3	
.0032	25	N/100 $AgNO_3$	8.20	8.15	.05
	25		8.10	8.10	
	25		8.20		
.0012	25	N/100 $AgNO_3$	2.95	2.80	.12
	25		2.80	2.75	
	25		2.95		

Discussion of Results.

An examination of the results contained in the preceding tables shows that these results can be divided into three characteristic groups, depending upon the acid radical. Thus, the adsorption of the hydroxides is much more marked than for any of the salts, while the adsorption of the carbonates is much greater than that of the chlorides and sulphates. This leads to the idea that possibly the adsorption observed is due largely to the presence of the hydroxyl ion, since even in solutions of carbonates a certain amount of hydrolysis occurs, resulting in the formation of the hydroxyl iron.

Shields (Ztschr. f. Phys. Chem. 12, 167, 1893,) has investigated the hydrolysis of a tenth-normal solution of sodium carbonate and finds it to be about 3% at 25° C. On the above supposition, therefore, the adsorption of a tenth-normal sodium carbonate solution and a three hundredth-normal sodium hydroxide solution should be the same. Reference to the data given above shows that the adsorption of a tenth-normal solution of sodium carbonate is about four times greater than could be explained on this

basis. This hypothesis cannot, therefore, explain the marked adsorption of the carbonates, although hydrolyses undoubtedly has some influence on the amount of adsorption.

The increased dissociation of the dissolved substance as the dilution increases gives an osmotic pressure-concentration curve somewhat similar to the experimental curve obtained, and suggests that the form of these curves arise from the fact that the osmotic pressure of the solution does not increase as rapidly as the concentration. In other words, that the amount of adsorption may be a simple function of the osmotic pressure of the solution. A comparison of the adsorption curve of potassium hydroxide, with its osmotic pressure-concentration curve, shows that the change in the slope of the osmotic pressure-concentration curve is entirely too small to explain the variation in the adsorption with concentration. It does not appear, therefore, that adsorption is directly proportional to the osmotic pressure of the solution.

Influence of Temperature on Adsorption by Powdered Quartz.

The apparatus used in investigating the influence of temperature on adsorption is shown in Figure 7. It consists of a copper tank 30 cm. wide, 35 cm. high and 60 cm. long carrying in its interior a brass shaft on which is mounted a series of racks for holding the bottles which contain the solutions. One end of the shaft rests in a bearing supported on a bracket which runs across the tank about 20 cm. from one end. The other end of the shaft passes through a stuffing-box in the opposite end of the tank and is provided with a light wooden pulley. The bottles containing the quartz and the solutions are held in the frame by suitable clamps. On slowly rotating the shaft, the solutions with the suspended material fall from one end of the bottles to the other, thus insuring thorough mixing. The bottles are completely covered with water, the temperature being regulated by a suitable thermostat. The shaft is driven by a low speed motor, the speed of which is further reduced by a series resistence.

Three series of determinations were made,- one at about

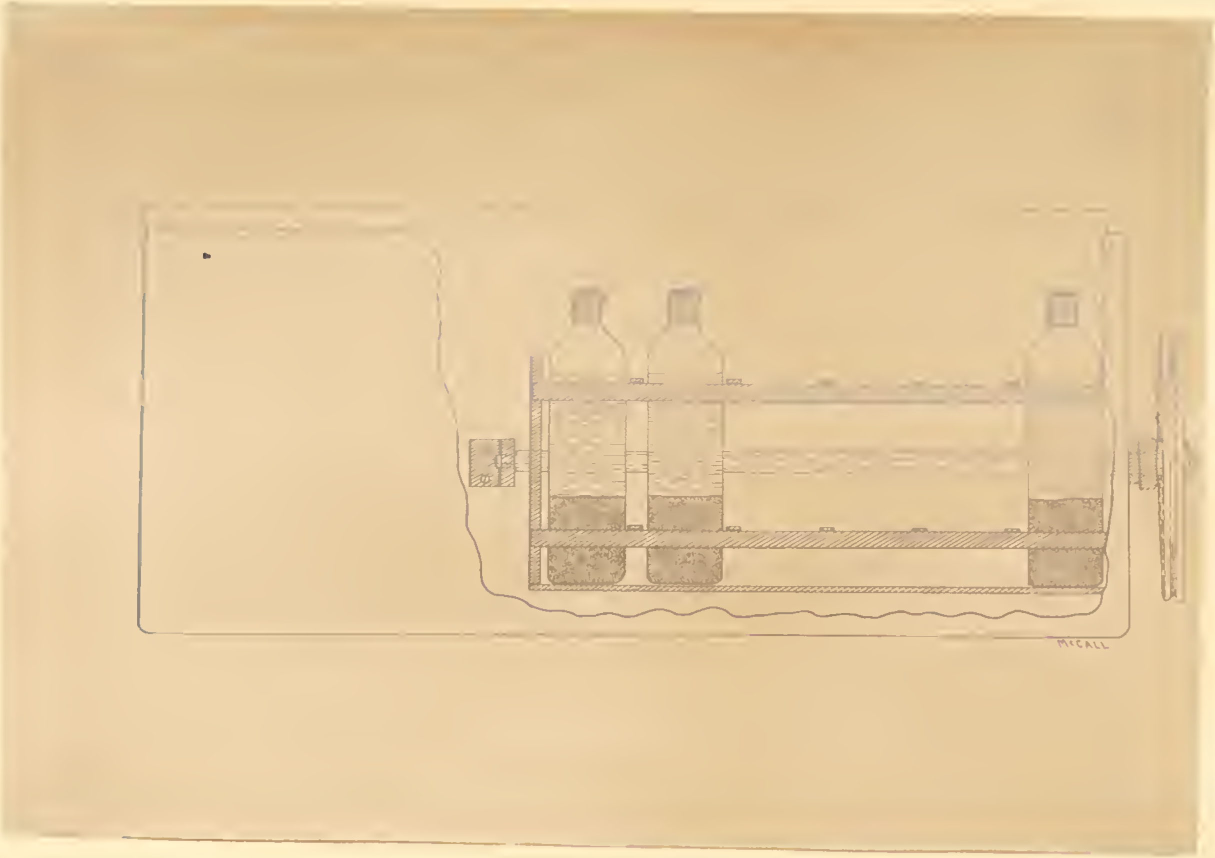


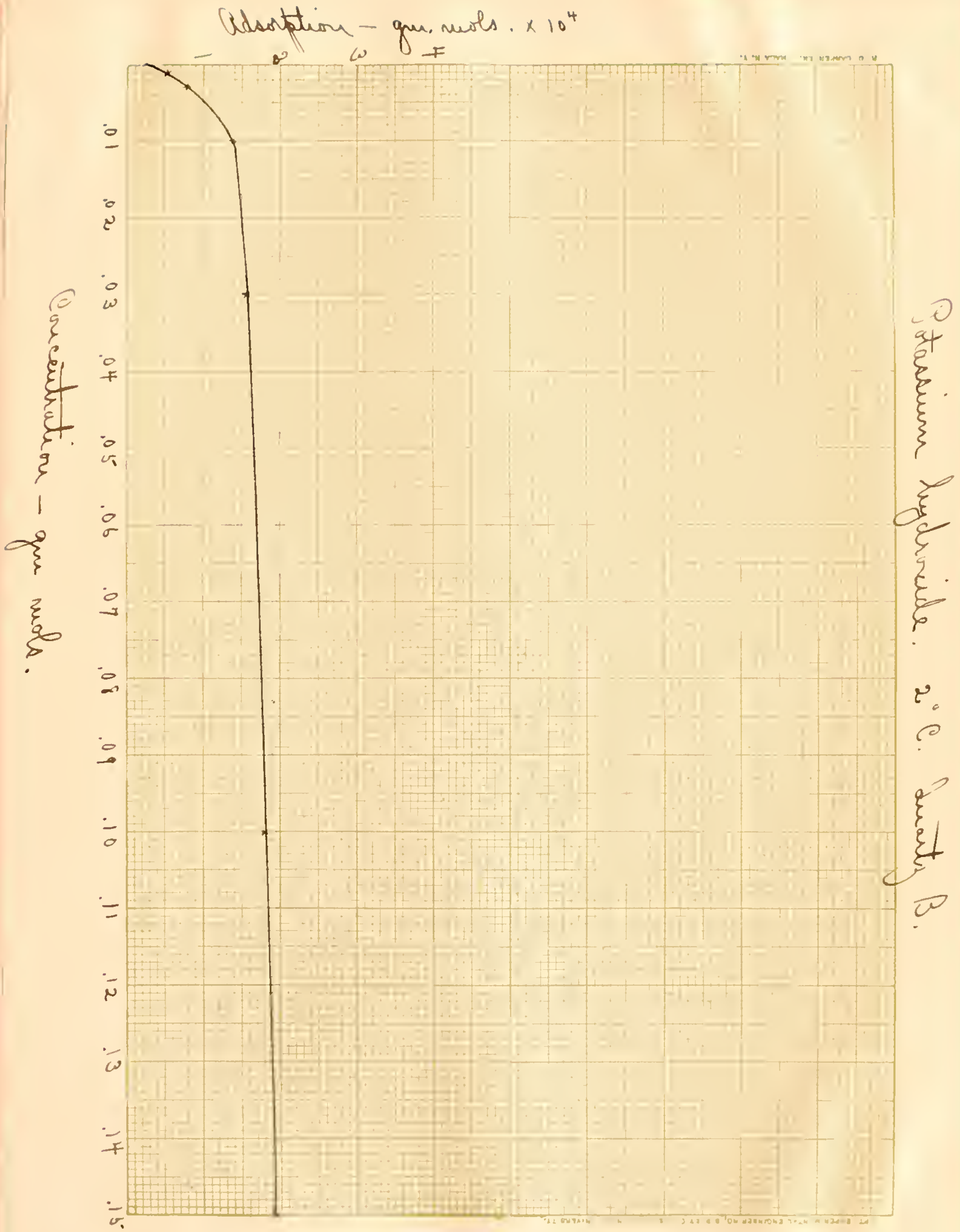
Fig 7 - Apparatus for investigating adsorption at constant
(temperature)

2°, one at room temperature, and a third at 40° C. In the determination at the lower temperature, the free space at one end of the tank was kept filled with ice, which secured a temperature of about 2° C. throughout, since the water was kept in thorough circulation by the movement of the shaft.

It is always necessary to allow some time for the suspended material to settle before the solution can be drawn off for analysis. In the experiments at 2o C., the bottles were held in an upright position in the tank, which was kept packed with broken ice for about twenty-four hours. Since at higher temperatures it is necessary to keep the shaft rotating in order to maintain the temperature constant through out the tank, the bottles were in this case removed from the rack and suspended under water in the free end of the tank. The powdered quartz, used in these experiments on the influence of temperature, does not contain as much fine material as that used in the earlier experiments. It has accordingly been designated as Quartz B, in distinction from Quartz A, used in the earlier work. The following tables give the adsorption observed at the three temperatures indicated, potassium hydroxide being the solution employed in all cases.

Potassium Hydroxide 2° C.

Concentration.	Amount titrated.	Titrating Reagent.	Amount titrating reag. required. Before ads.	After ads.	Mean difference.	Total absorption.
0.1825	25 cc.	N/10 HCl	46.0	45.65		
			45.9	45.60	0.35	2.10 x 10^{-4}
			46.0			
0.0910	25 cc.	N/10 HCl	23.05	22.75		
			23.04	22.75	0.30	1.80
			23.08			
0.0297	25 cc.	N/10 HCl	7.70	7.45		
			7.70	7.42	0.26	1.56
			7.70	7.42		
0.0092	25 cc.	N/100 HCl	25.40	23.0	2.42	1.45
			25.51	23.1		
			25.50			
0.0029	25 cc.	N/100 HCl	8.57	7.0		
			8.60	7.5	1.34	0.80
			8.61			
0.0007	25 cc.	N/100 HCl	2.85	1.70		
			2.83	1.80	1.09	0.65
			2.83			



Potassium hydroxide. 2°C. Charcoal B.

Potassium Hydroxide 20° C.

Concentration.	Amount titrated.	Titrating Reagent.	Amount titrating reagent required.		Mean difference.	Total Adsorption.
			Before ads.	After ads.		
0.0728	25 cc.	N/10 HCl	18.65	18.22		
			18.60	18.20	0.415	2.49×10^{-4}
0.0233	25 cc.	N/10 HCl	6.10	5.82		
			6.10	5.85	0.265	1.59
0.0071	25 cc.	N/100 HCl	18.60	17.86		
			18.60	17.80	0.77	0.46
0.0024[1]	25 cc.	N/100 HCl	6.65	6.08		
			6.70	6.06	0.60	0.31
0.0007	25 cc.	N/100 HCl	2.15	1.73		
			2.10	1.72	0.40	0.24

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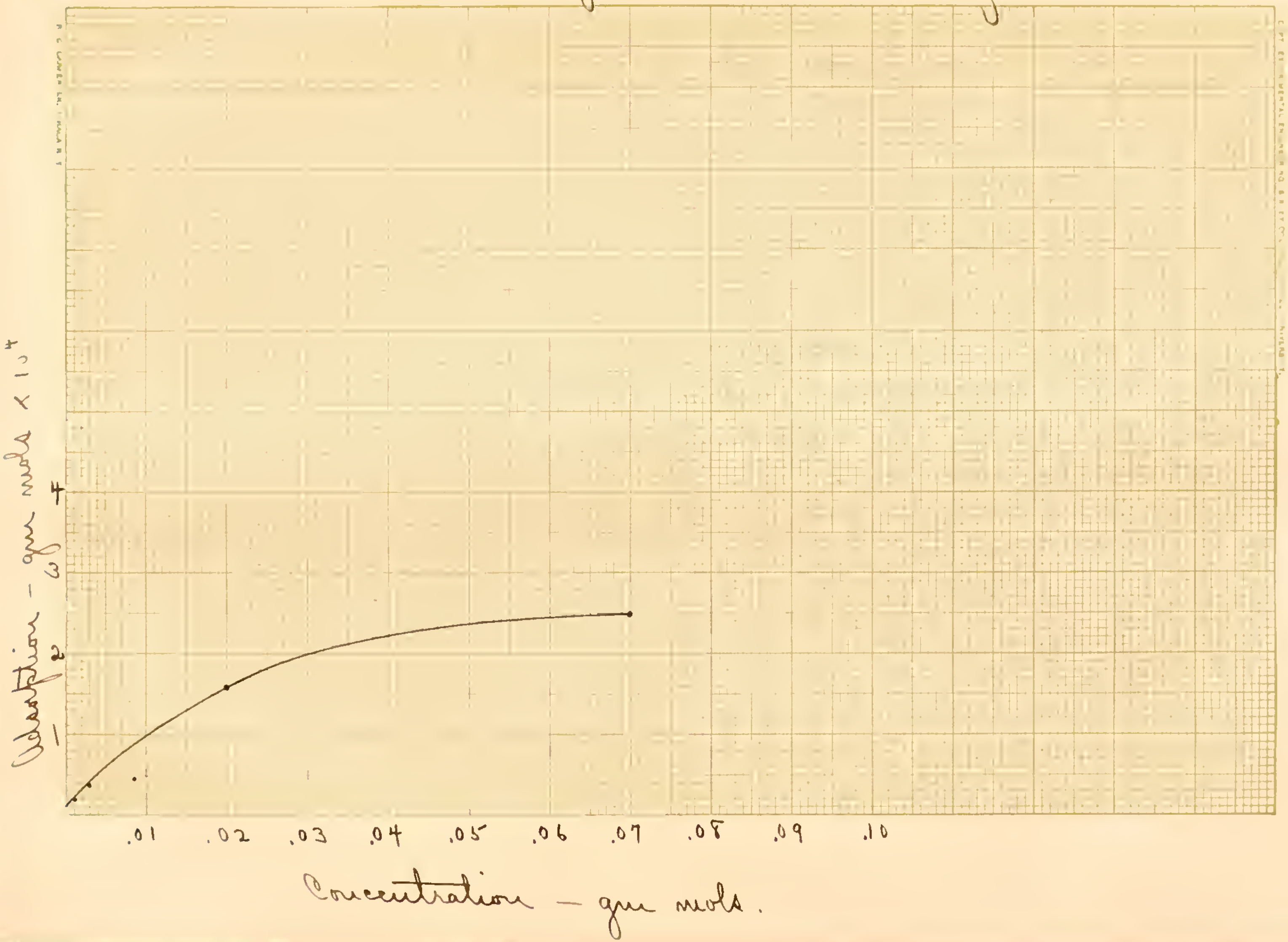
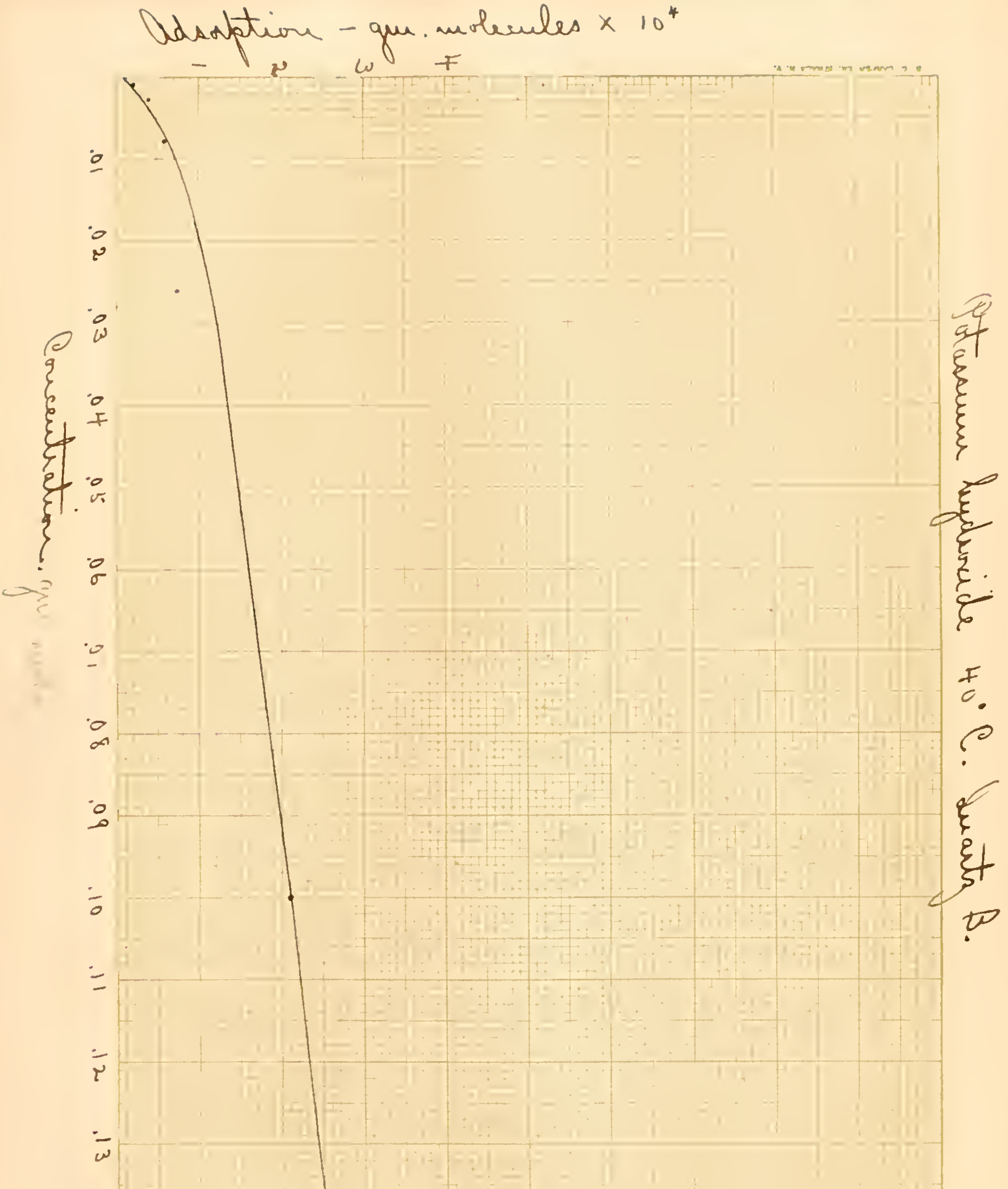
[1] Only 130 cc. instead of 150, as usual.

Potassium Hydroxide 20°C. Quartz B.



Potassium Hydroxide at 40° C.

Concentration.	Amount titrated.	Titrating Reagent.	Amt. titrating reag. required		Mean difference.	Total adsorption.
			Before ads.	After ads.		
.1884	cc.				cc.	
	25	N/10 HCl	47.58	47.04	0.55	3.30 x 10^{-4}
	25		47.60	47.05		
.09976	25	N/10 HCl	25.26	24.84	0.35	2.10
			25.20	24.92		
.02634	25	N/10 HCl	6.60	6.51	0.12	0.72
	25		6.65	6.54		
.0077	25	N/10 HCl	19.65	18.70	0.975	0.58
	25		19.70	18.70		
.0009	25	N/100 HCl	2.10	1.75	0.35	0.21
			2.10	1.75		
.0026	25	N/100 HCl	6.60	5.85	0.775	0.46
	25		6.63	5.83		


Adsorption - gm. molecules × 10⁴
1
2
3
4
Potassium hydroxide 40° C. Quartz B.
Concentration, gm.
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
.11
.12
.13
.14
.15

Determination of Adsorption by the Conductivity Method.

Kellner's investigations on the adsorption of very dilute acid and alkaline solutions by platinum black, employing the conductivity method, has already been noted. This method is not, howeever, more accurate than titration methods, except for very dilute solutions. It is, nevertheless, valuable where suitable titration methods do not exist, as in the case of the sulphates, and some investigations on the adsorption of sodium sulphate by quartz have been made. A sample of quartz was washed by means of the apparatus shown in Figure 3 until the electrical resistance of the filtrate in the Arrhenius cell employed was about 40,000 ohms. The quartz was then dried and saturated with a hundredth normal solution of sodium sulphate. This was allowed to stand in contact with the quartz for about twenty-four hours, when it was thrown out by centrifugal action, using the apparatus shown in Figure 6, and the conductivity of the solution determined. It was found to be 82 ohms at 25° C., which agreed with the conductivity of the original solution to within the experimental error.

Other determinations gave similar results. Therefore, we seem justified in concluding that the adsorption of sulphates by quartz is of the same order as was found for the chlorides.

This method of simply filling the interstitial space of the quartz with the solution under investigation has the great advantage of confining the adsorption to the smallest possible amount of water, and therefore increasing in a corresponding manner the differences observed. It is proposed to continue the investigations on adsorption by this method, making direct titrations when possible and conductivity measurements in special designed cells when titrations are not feasible.

Conclusions.

From the investigations described in this paper, the following conclusions can be drawn:-

1. The amount of adsorption in the case of solutions of carbonates and hydroxides is not directly proportional to concentration, if we take into consideration adsorption

at very small concentrations.

2. The amount of adsorption is relatively much greater in very dilute solutions, the ratio of the amount of salt adsorbed to the concentration decreasing as the concentration increases.

3. Above concentrations of about two hundredth-normal, the ratio of the amount of adsorption to the concentration remains practically constant up to concentrations of one-tenth or one-fifth normal, which were the greatest concentrations employed. This portion of the curve agrees with the results obtained by van Bemmelin and Schmidt, who worked with corresponding concentrations.

4. The adsorptions of the various salts investigated appears to be a function of the acid radical rather than of the basic element, the sodium, potassium and ammonium salts of any given acid showing no characteristic differences in the amount of adsorption.

5. The amount of adsorption of the several hydroxides is approximately four times the adsorption of carbonates for equal concentrations.

6. The adsorption occurring in solutions of chlorides or sulphates is only about one eighth as great as that occurring in the case of carbonates, or one thirtieth of that occurring with hydroxides of equal concentration.

Biographical.

Lyman J. Briggs was born in Barry county, Michigan, May 7, 1874. He entered the Michigan Agricultural College in 1889, and received the degree of Bachelor of Science in 1893. The two following years were spent at the University of Michigan, where he received the degree of Master of Science in 1895, in Physics as a principal subject and Mathematics and theoretical Mechanics as subordinate subjects.

He entered Johns Hopkins University in the autumn of 1895, where he remained one year, with Physics as a principal subject and Physical Chemistry and Mathematics as subordinate subjects. At the close of the University year he was appointed physicist in the United States Department of Agriculture, and in January, 1898, was made assistant chief and physicist of the Division of Soils, which position he now holds.

In October, 1900, he was granted permission by the Secretary of Agriculture and by Professor Milton Whitney, Chief of the Division of Soils, to continue his work at this University. He was appointed Fellow by Courtesy for the cur-

rent academic year. He married Miss Katherine E. Cook, of Claremont, California, in December, 1896.